THE CHEMISTRY OF THE SALTS OF STRONG ACIDS.

by

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ABSTRACT.

Solutions of the First Row Transition Metal salts of some strong acids (perchlorates, trifluoro-acetates and tetrafluoroborates) have been prepared in non-aqueous solvents viz. ether, benzene and nitromethane. Two methods of preparation have been employed.

1. Dehydration of the hydrates.

Hydrated salts of the above acids were prepared by adding excess transition metal oxide, hydroxide or carbonate to an aqueous solution of the strong acid. Recrystallisation was carried out to ensure purity.

Dehydration has been attempted by thermal decomposition using a thermogravimetric balance. In many cases, water was completely removed but some decomposition of the anhydrous strong acid salt accompanied the dehydration. The decomposition products e.g. fluorides and chlorides were insoluble in the organic solvents used and solutions could be prepared from the mixtures produced after the dehydration stage.

Removal of water using 2,2 dimethoxypropane has also been attempted. Excess of the reagent was added to the hydrate and the mixture stirred for varying periods of time. The reaction proceeded according to the equation :-

$CH_3C(OCH_3)_2CH_3 + H_2O = 2\ CH_3OH + (CH_3)_2CO$.

Anhydrous compounds again gave solutions although some doubt exists, due to the decomposition products of the dimethoxypropane, as to the exact nature of the solvent system.

2. Metathesis.

The anhydrous silver salt of the strong acid was dissolved in the organic solvent and excess anhydrous metal halide or metal added. After some time, ranging from one week to two months, the silver halide or silver metal was completely precipitated producing a solution of the transition metal salt.

For the dipositive metals, two distinct species have been identified in solution corresponding to the formulae $M(Cl)X$ and MX_2, where X is the strong acid anion. In the tripositive series, the evidence points to the formula MX_3 only.

Solutions prepared from the dehydration reactions were similar to those obtained for the MX_2 or MX_3 types. Metals studied were :- zinc (11), copper (11), titanium (111), vanadium (111), chromium (111), iron (11), iron (111), nickel (11) and cobalt (11).

The solutions have been examined by means of ultra-violet and near infra-red spectroscopy, magnetic and conductivity measurements and by analysis. Solid trifluoroacetates, both in ' chloro-' and ' bis ' forms have been obtained in the divalent series. Only the ' tris ' compound could be isolated from the trivalent metal solutions. These solids resulted from the removal of solvent from nitromethane solution and were studied by similar methods to those used for solutions. Attempts to prepare the anhydrous compound from perchlorate and tetrafluoroborate solutions always resulted in considerable decomposition in the latter stages of solvent removal.

The results have established that the compounds formed in solution are weak-field, octahedral complexes in which the solvent occupies at least

two of the coordination positions round the central metal atom and in which there is considerable anion-cation interaction.

Some attempts have been made to prepare solid, strong acid salts of some Group VA trivalent elements by metathesis involving the anhydrous silver salt and the halide as before. Quantitative precipitation of silver halide resulted, but in some cases the solid compound could not be isolated in a pure state.

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INTRODUCTION

Non-aqueous solvents have been used as media for inorganic reactions for many years. It was not until the turn of the century, however, that a systematic investigation of their uses was carried out by Franklin and Kraus (1) in America and Walden (2) in Russia. Even after this, inorganic chemists were slow to make use of such solvents and work in this field was considered rather 'exotic'. In the past twenty-five years there has been a remarkable increase in the interest shown in non-aqueous solvents as demonstrated by the considerable increase in the number of publications devoted to the subject.

It is generally accepted that water occupies a special place as a solvent in its ability to dissolve substances of a wide variety of types, structures and compositions. Its availability, physical properties (including liquid range) and solvating properties have caused much attention to be devoted to the 'universal solvent'. Early theories on chemical and physical behaviour in solution were restricted to aqueous media and this undoubtedly encouraged its continued use for most inorganic reactions.

Since the work of Franklin, Kraus and Walden up to the present day, it has become increasingly apparent that, although water is an excellent solvent, it is not unique. The increasing interest in non-aqueous solvents has resulted in their application to a wide variety of problems e.g. the study of solutions of compounds which are readily hydrolysed by water, the preparation of metal complexes with organic ligands which are insoluble in water and in numerous inorganic syntheses.

While early work in non-aqueous solvents was mostly restricted to inorganic liquids such as liquid sulphur dioxide, liquid ammonia and sulphuric acid, the chemical properties of these solvents made them somewhat undesirable in view of the experimental difficulties accompanying their use. The emphasis shifted, therefore, to organic solvents such as alcohols, ether and amines, and, although toxicity remained something of a problem, they were, in general, more easy to handle.

Classification of solvents is a difficult task since the vast multiplicity of solvent properties makes a division, which would be satisfactory to all chemists, almost impossible.

Several attempts have been made to group solvents. One such classification places solvents in four classes as follows:-

1. Acidic solvents having a strong tendency to donate a proton to a proton acceptor. Examples are sulphuric, trifluoroacetic acids and hydrogen fluoride.

2. Basic solvents which will readily accept a proton. In this group fall solvents which contain an electron pair available for donation, e.g. aliphatic amines, ethers, thioethers. Aromatic compounds may be included here, acting as donors through their π electrons. Many basic solvents act as co-ordinating agents to metal ions.

3. Amphiprotic solvents act either as acidic or basic solvents depending on the nature of the solute dissolved. Water and the lower alcohols fall into this class.

4. Aprotic solvents behave neither as acidic nor basic solvents, acting generally as inert reaction media, e.g. halogenated hydrocarbons.

It would be erroneous to assume that this classification covers all cases or indeed that one solvent would fall into the same class regardless of the reaction involved.

Since the inorganic chemist is often concerned with ions in solution, solvent-ion interaction is important in classifying a solvent. Division into polar and non-polar types, with the arbitrary lines around a dielectric constant of 25-30, is a common grouping. This is based on a purely electrostatic consideration which is an important, but not the sole, factor. Thus, on the basis of solvent-solute interaction, it is possible to arrange solvents into the following four groups:-

1. Polar electron donors. These are the most efficient solvents, combining high dielectric constant with the ability to solvate. Examples are water, acetonitrile, nitromethane.

2. Non-polar electron donors. While these solvents have comparatively low dielectric constants, they are capable of dissolving many inorganic substances due to their ability to form complexes with the metal ion. This is achieved by either π or σ bonding. Pyridine, benzene, aniline and ether belong to this group.

3. Polar non-donors. These possess high dielectric constants yet are very weak electron donors, in many instances acting as electron acceptors. The metal ion is largely unsolvated in such liquids since the solvent has no co-ordinating properties. These solvents are acidic e.g. formic acid, and neutral e.g. nitrobenzene.

4. Non-polar non-donors. This group includes many solvents of low dielectric constant and many which do not fall into the first three categories, e.g. chloroform, carbon tetrachloride.

The selection of an appropriate solvent is governed by whether the interest of the investigator lies in the solvent properties of a particular liquid or in a chemical reaction for which the most suitable solvent must be found. The solubility of a salt in a given solvent is governed by the extent to which the total solvation energy of the ions outweighs the work done in breaking the ionic lattice. For many years it was considered that a high dielectric constant was a necessary property of a good solvent. The electrostatic interaction of the ions will be greatly reduced by a highly polar solvent.

On the basis of present-day knowledge, it is realised that this is only one aspect of the problem. Many solvents with low dielectric constant are known to be good solvents for inorganic salts. Remarkable solvent properties are shown by liquids which contain atoms having an unshared pair of electrons. Thus ethers, ketones and amines are good solvents while saturated hydrocarbons show no comparable solvent properties. It is therefore reasonable to infer that the possession of lone pairs of electrons is an important factor. The ideal requirements for a salt to be soluble in ethers, ketones or amines, are:- (i) a very small cation (of high polarising power) and/or (ii) a low lattice energy, which is evident in salts with large anions. Thus sodium iodide, lithium perchlorate and tetrafluoroborate dissolve in organic solvents.

It has been shown that many silver salts are soluble in unsaturated or aromatic hydrocarbons (3, 4) and these solvents possess π bonding systems e.g. silver tetrafluoroborate is soluble in benzene and toluene (5).

The corresponding sodium and potassium salts are insoluble in these solvents although they have similar ionic radii (Ag^+ 1.0Å, Na^+ 0.98Å, K^+ 1.33Å). Thus the solubility of the silver salt must be more complex than a mere polarising effect.

That π electrons can be used in bonding is adequately established by the numbers of this type of complex known. Silver and the first-row transition metals studied in this project all possess d orbitals which are filled or partially occupied. Although the sodium and potassium salts have vacant d orbitals, these are of unsuitable energy for bonding. Thus the solubility of silver and transition metal salts in aromatic solvents can be attributed, in part, to the possession of d electrons.

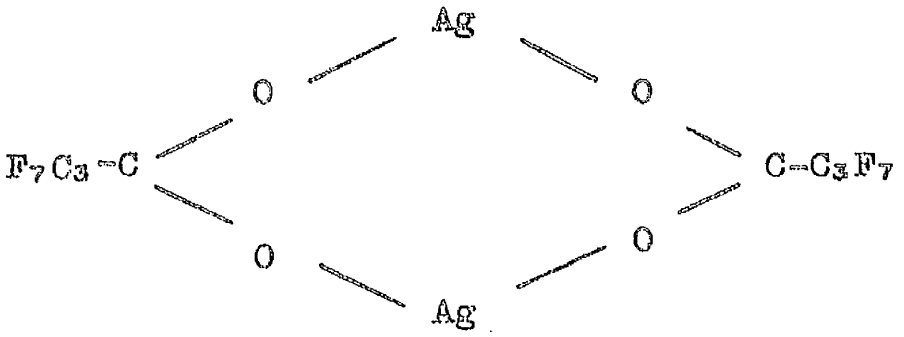
Silver Salts of Strong Acids

X-ray and infra-red studies of silver perchlorate (6) have shown that the compound is ionic in the solid state. From conductivity and molecular weight measurements in benzene (3) it has been concluded that the salt is monomeric at low concentrations. As the concentration increases, polymerisation takes place to some extent. The conductivity of these solutions indicates that aggregation of ion-pairs occurs as the solution increases in strength. It is always conceivable, however, that there may be covalent bond formation between the silver ion and an oxygen atom of the perchlorate group, especially at high concentrations. Covalent bonds can also be formed with the oxygen atom of the carboxyl group of perfluorocarboxylic acids such as trifluoroacetic acid.

The silver salts of complex fluoroacids have been shown to be ionic by X-ray and infra-red studies (4). Thus silver tetrafluoroborate is isomorphous with the potassium salt and has an identical infra-red spectrum. In order to consider silver tetrafluoroborate as a covalent compound, it would be necessary to propose that bond formation involves either bivalent fluorine or bond formation between

the silver ion and the central atom of the anion. Sharpe (7), however, has pointed out that the unknown acid, HBF_4, cannot be formulated without postulating quinquevalent boron or bivalent fluorine. Neither of these possibilities is likely since the boron does not contain d levels of a suitable energy. The maximum co-ordination number of the boron is therefore four. Fluorine does not normally form a covalent link betwen two atoms except in condensed anions (7). The failure of hydrogen fluoride and boron trifluoride to combine in equimolecular proportions is therefore understandable. It is reasonable to suppose that combination will only occur when an electron donor, which will solvate the proton, is present e.g. ammonia to give $NH_4^+ BF_4^-$, benzene to give $C_6H_7^+ BF_4^-$.

Information on the trifluoroacetates is not so complete but it is evident, from X-ray powder photographs, that the silver and potassium salts are markedly different. A complete structural determination has been carried out on silver heptafluorobutyrate (8). This shows that the compound exists as a dimer, each silver atom being part of a chelate ring.



Silver Heptafluorobutyrate

It is quite possible that such a structure is present in silver trifluoroacetate, but most unlikely in the potassium salt, since the latter ion is unable to utilise suitable orbitals. The infra-red spectrum of silver trifluoroacetate lends weight to the suggestion that the salt is covalent since it is very similar to that of silver heptafluoro-butyrate and noticeably different from that of potassium trifluoroacetate (4).

In considering the perchlorate and tetrafluoro-borate as ionic, it is necessary to assume that bonding in aromatic hydrocarbon solutions involves the silver ion and the aromatic system. The nature of such a complex has been discussed by Mulliken (9). This treatment considers the donation of π electrons from the aromatic system to vacant orbitals on the metal ion. Structurally, the possible positions of the silver ion are:-

(i) above the centre of the benzene ring,

(ii) above one bond in the ring,

(iii) above one corner of the ring.

A 'sandwich' structure of the silver ion between two benzene rings was disregarded although this type of structure is now well established.

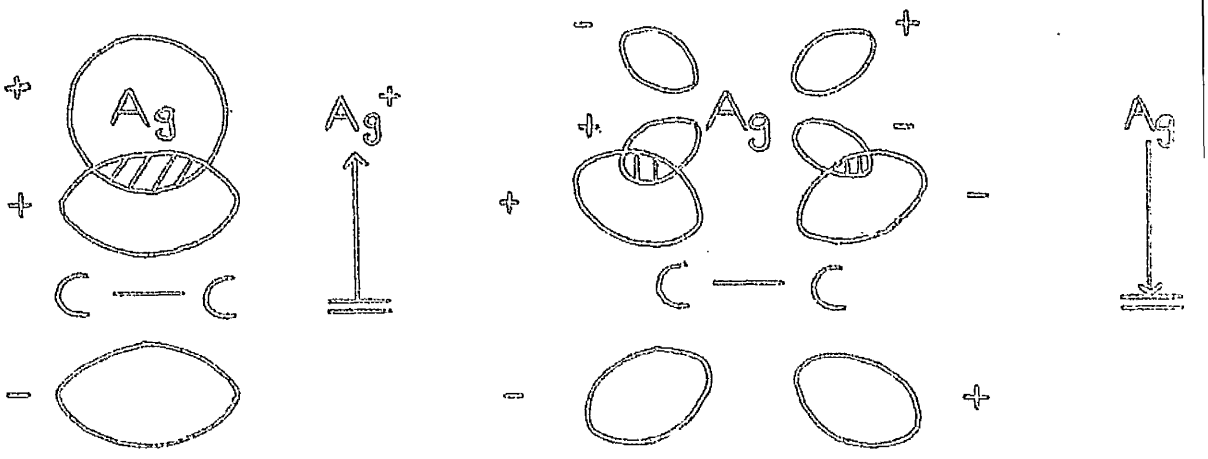
Mulliken, considering symmetry conditions, excludes the centrosymmetric model (i) on the grounds that such an interaction would involve considerable electronic excitation. Similar reasoning, together with geometrical problems, have caused structure (iii) to be discarded. The model favoured by Mulliken is thus the form in which the silver ion is above one of the C-C bonds. X-ray crystal structural determinations of the $AgClO_4 . C_6H_6$ complex published in two papers (10, 11) have supported this theory. The conclusions reached by these authors are that the silver ion is situated above one of the C-C bonds but slightly to one side, and that the benzene ring is distorted. The C-C bond associated with the silver ion is reduced in length from 1.43Å to 1.35Å. Each benzene ring is bonded to two silver atoms and each silver atom to two benzene rings.

The Raman spectra of benzene solutions of silver perchlorate have been studied (12). It was observed that for the totally symmetrical C-C vibration a frequency shift of 13cm^{-1} was obtained. This is smaller than the shift recorded for the corresponding olefine complexes ($\sim$ 60-70cm^{-1}) and acetylene complexes ($\sim$100cm^{-1}). It may be deduced therefore that the influence of the silver ion is directed towards more than one double bond. It is unfortunate that many of the anhydrous silver salts of strong acids are not sufficiently soluble in aromatic hydrocarbons to give reliable Raman spectra.

The Mulliken concept of the bonding in the $AgClO_4 . C_6H_6$ complex does not take into account the bond energy. It is to be expected that this would be fairly small, in common with other similar types of charge-transfer complex. The bond energy in the iodine-benzene complex is given as $\sim$ 2k. cals. (13). Rundle and Smith (10) estimate the bond energy of the silver-benzene complex as 15.7 k. cals. while Tildesley and Sharpe (15) give a value of $\sim$ 50 k. cals. The predicted charge transfer band at 2300Å (16) for the complex has not been observed since there is 100% absorption for the aromatic hydrocarbon in that region (17).

Steric factors appear to play no important role in such complexes. Mulliken (9) has tried to relate the stability of the 1:1 complexes formed between substituted aromatic hydrocarbons e.g. benzene, mesitylene and the xylenes, and silver ions in aqueous solution. He concludes that steric hindrance of the methyl group is an important factor in the stability of these complexes. This has been contradicted by Tildesley and Sharpe (18) who demonstrated the solubility of silver heptafluorobutyrate in solutions of durene and hexamethyl-benzene in cyclohexane, and by Sharp (4) who showed that silver hexafluorophosphate was soluble in mesitylene. It is obvious that steric hindrance is very large in such cases thus some other factor must be considered in the bonding.

From the evidence of Andrews and Keefer (19), it would appear that the 1:1 silver-benzene complexes are fairly stable. The high bond strength may be explained in terms of back-bonding from the metal ion to the benzene ring, donation occurring between d orbitals on the silver ion to the antibonding π^{*} orbitals of the benzene molecule.



This would allow a symmetrical model for the complex since excited orbitals can now be involved in π bond donation. Such back donation was postulated by Chatt (20) to account for the formation of platinum - olefine complexes when trimethylborane - olefine complexes do not form.

The 5 s orbital on the silver ion is capable of accepting electrons from the π^* orbitals of the benzene and the metal can donate electrons from the filled 4 d level into the π orbitals of the benzene ring. This would explain the insolubility of sodium and potassium perchlorate and lithium tetrafluoroborate in aromatic hydrocarbons. On the other hand, it could account for the solubility of first-row transition metal perchlorates and tetrafluoroborates

in aromatic solvents, since these ions also have d orbitals.

The bonding in ether and nitromethane solutions appears much less complicated to understand. Donation of the lone pair of electrons on the oxygen atom to the metal would form an approximately covalent link and thus stabilise the complexes.

Sharp (4) used solutions of silver tetrafluoroborate in aromatic hydrocarbons in attempts to prepare tetrafluoroborates of other metals. When the silver solution was shaken with copper powder, silver was displaced from solution. By this means, a solution of cuprous tetrafluoroborate was obtained. Using similar reactions, cuprous fluorosulphate, hexafluorophosphate, -arsenate, -niobate and -tantalate were prepared in solution. No solid samples could be isolated, decomposition occurring as solvent was removed. This work was extended to other metals. It was found that, although zinc, lead, thallium, mercury, aluminium (amalgam) and chromium all displaced silver from silver tetrafluoroborate solution, no metal ion entered solution. No displacement occurred using gold, aluminium, magnesium and nickel.

Monnier (21) prepared solutions of iron (11) cobalt (11), nickel (11), copper (11) and zinc (11) perchlorates in ether by metathesis between the metal bromide and silver perchlorate. On filtration to remove silver bromide, Monnier states that any excess halide was removed by additions of silver perchlorate in ether. This is very significant in the light of the results of this project.

In the present work, a systematic study of the solutions of first-row transition metal salts of strong acids has been made. The solutions were prepared by the method of Monnier (21). The solvents used were diethyl ether, benzene and nitromethane. These were chosen to give a range of solvent properties. The following table shows some of the properties previously described as being important in this section.

	Ether	Benzene	Nitro-methane
Dielectric Constant	4.4(20°C)	2.3(25°C)	35.8(30°C)
Classification			
(a)	Basic	Basic	Basic
(b)	Non-polar Electron Donor	Non-polar Electron Donor	Polar Electron Donor
Bonding Type	σ	π	σ

As a general statement, the perchlorates, trifluoroacetates and tetrafluoroborates of first-row transition metal elements are soluble in the solvents chosen. Bonding in the complexes formed in solution must be similar to the bonding previously described for silver salts.

CHAPTER I

The Preparation of Solutions of First-Row Transition Metal Salts of Strong Acids in Some Non-Aqueous Solvents.

It is becoming more apparent, as modern research expands, that the use of non-aqueous solvents in the examination of inorganic species in solution and in the preparation of otherwise unobtainable anhydrous compounds, is of great importance. Many new compounds, which cannot exist in aqueous solution, are readily obtained in a stabilised form in the absence of water. The properties of an anhydrous compound and those of the hydrated form can be remarkably different e.g. cupric nitrate (22) and perchlorate (23), both of which can be sublimed under vacuum. Neither compounds can be obtained from the hydrates by thermal dehydration, decomposition accompanying the removal of water.

It must be stressed that inorganic compounds which are crystallised from organic solvents very frequently contain solvent of crystallisation. In some cases removal of such solvent molecules is extremely difficult if decomposition of the desolvated compound is to be avoided. One requirement of paramount importance in the use of non-aqueous solvents is that the solvent must be scrupulously anhydrous.

The chemical reactivity of many solvents is remarkably altered by the presence of even small amounts of water.

The solubility of inorganic compounds in non-aqueous solvents depends on a number of factors. These are discussed in the cases of the solvents used in this section.

1. Aromatic Hydrocarbons

The low lattice energy of covalent molecular salts renders solubility in aromatic hydrocarbons a distinct possibility. The small solvation energy will adequately compensate for the weak Van der Waals forces which hold the lattice together. Both mercurous trichloro - (24) and trifluoroacetates (25) dissolve in benzene. Examination of the dipole moment of the former compound favours a simple covalent species in solution, the $Cl_3C.CO$ groups rotating round the O-Hg-Hg-O axis.

A large number of silver salts of strong acids have been found to be soluble in aromatic hydrocarbons. The solubility of silver perchlorate in benzene, toluene and chlorobenzene was studied by Hill (3).

The degree of electrolytic dissociation was found to be very small, of the same order as that of water, having a specific conductance of 7.4×10^{-7} Ωhm^{-1} cm^{-1} compared to a value of 6×10^{-8} for good conductivity water. Silver perchlorate is also soluble in m-xylene but insoluble in chloroform and carbon tetrachloride. Spurgeon (26) isolated a stable complex from benzene ($AgClO_4.C_6H_6$) and reports the formation of a similar complex ($AgClO_4.C_7H_8$) in toluene. Peyronel et al. (27) prepared a whole series of silver perchlorate - hydrocarbon complexes involving the xylenes and some polynuclear hydrocarbons. All of these compounds are extremely hygroscopic.

Silver trifluoroacetate and heptafluorobutyrate are also soluble in aromatic hydrocarbons and complexes between these salts and benzene, toluene, mesitylene and the xylenes have been characterised (25, 18.) Silver trifluoro-methylsulphonate (29), trifluoromethyl antimonate, bistrifluoromethylphosphinate (30), and trichloroacetate (24) have been reported soluble in benzene although in the case of the trichloroacetate, decomposition occurs rapidly in solution with the precipitation of silver chloride.

Evidence for the formation of complexes between silver salts and aromatic hydrocarbons has been found by Andrews, Keefer et al. A great deal of attention has been directed towards the solubility of aromatic hydrocarbons and their alkyl derivatives in aqueous silver nitrate (31). The ionic species $AgAr^+$ and Ag_2Ar^+ are formed and the order of stability of these complexes follows the order of the hydrocarbons when considered as electron donors. This complex formation has been used (32) to separate the xylenes and ethyl benzene, the complex with ethyl benzene being much less stable than the others.

Warf (33) has shown that silver tetrafluoroborate monohydrate dissolves in benzene and toluene. It is not known if the hydrate dissolves with the water molecule still attached to the silver ion. The same author prepared a solution of silver tetrafluoroborate by passing boron trifluoride through a suspension of silver fluoride in toluene. A similar preparation (34) using benzene, resulted in the isolation of the complex $AgBF_4 \cdot C_6H_6$, from which the pure tetrafluoroborate was obtained by decomposition at 50°C/1mm.. Sharpe (5) had first

prepared the pure compound by treating silver borate with bromine trifluoride and demonstrated its solubility in ether, benzene and toluene, thus establishing a marked similarity between this salt and silver perchlorate. Russell and Sharp (35) have shown that silver tetrafluoroborate and hexafluorophosphate can be prepared by passing the appropriate gas through a suspension of silver fluoride in liquid sulphur dioxide.

The solubilities and general properties of perchlorates and hexafluorophosphates are very similar (36). Sharp and Sharpe (37) have shown that this resemblance extends to the solubility of the hexafluorophosphate in aromatic hydrocarbons. Moss (38) showed that some silver salts containing two silver atoms per molecule e.g. silver hexafluorosilicate and hexafluorotitanate, dissolved to a small extent in ether, benzene and toluene. The lattice energy of these salts with divalent anions will be much greater than for univalent anions and this would lead to a reduction in solubility.

It may be considered that complexes form between silver ions and aromatic hydrocarbons because of the ready availability of π electrons on hydrocarbon. Thus it is to be expected that silver ions would form olefine derivatives. These are well known, although mainly in aqueous solution. Using partition studies, Eberz et al. (39) have shown the existance of very stable complexes. Thus with isobutene, $C_4H_8Ag^+$ is formed. Comyns and Lucas (40) prepared the cyclohexene derivatives of silver nitrate and perchlorate. The latter salt also reacts with α and β pinene giving compounds of the formula $AgClO_4 . {}^2C_{10}H_{16}$. Stable silver complexes with olefines have been described by Quinn and Glew (41). Working at room temperature and low pressure, derivatives of silver tetrafluoroborate have been prepared. Perchlorate and hexafluoro-antimonate complexes with propylene are also described, the order of stability being:-

$$ClO_4^- < BF_4^- < SbF_6^-$$

The separation of ethylene from saturated hydrocarbons (42) and styrene from similar mixtures (43) using silver tetrafluoroborate, is the subject of two recent patents.

Recently the absorption of ethylene by silver tetrafluoroborate and silver nitrate has been studied (44).

In general, cuprous olefine complexes are more stable than the corresponding silver compounds. Addition compounds of cuprous chloride are formed with ethylene, propylene and isobutylene under pressure (45). Andrews and Keefer have prepared water-soluble complexes of cuprous ions with unsaturated alcohols and carboxylic acids, in which it must be assumed that the metal interacts with the double bond rather than the hydroxyl group. It is suggested that the stability of the bond is dependent on the steric influence of groups attached to the double bond, although such steric factors do not appear significant with aromatics.

Warf (33) prepared a complex of a copper salt, cuprous tetrafluoroborate, in benzene and toluene by refluxing aryldiazonium tetrafluoroborates in these solvents with metallic copper. The same author reported the preparation of silver and cuprous tetrafluoroborate solutions by passing boron trifluoride through suspensions of silver fluoride and mixtures of copper metal and cupric fluoride

respectively, in toluene.

A solution of cuprous nitrate was prepared by shaking a solution of silver nitrate in acetonitrile with metallic copper (47). Sharp and Sharpe (37) adapted this method to prepare solutions of cuprous tetrafluoroborate, fluorosulphate, hexafluoro - phosphate, - arsenate, - niobate and - tantalate in aromatic hydrocarbons. These solutions are stable in the absence of moisture although no solid complexes could be isolated. Comyns (48) reported similar results when solutions of silver perchlorate in olefines and disubstituted acetylenes were treated with copper, the cuprous salts again being stabilised in solution.

A review by Andrews (49) covers some of the evidence for complex formation between inorganic compounds and aromatic hydrocarbons. Much of the work published concerns the halides of metals which may be considered as Lewis acids i.e. electron acceptors e.g. ferric and aluminium halides. A solution of aluminium bromide in benzene dissolves potassium bromide to give a conducting solution (50).

Similar results were obtained by the same authors using toluene, o- and p-xylene (51). It seems likely that bonding to the anion takes place in such complexes.

Aluminium perchlorate has been prepared by reacting aluminium chloride and silver perchlorate in benzene (52), the anhydrous salt being obtained by removal of the solvent. Salts of gallium in aromatic hydrocarbons have also been studied. Gallium dichloride merited special attention because of the anomalous valency state. Magnetic studies showed the compound to be diamagnetic (53) and a Ga-Ga bond was postulated. X-ray structural determination (54) and Raman spectroscopy (55, 56) established the structure as $[Ga^{I}]^{+}\ [Ga^{III}Cl_4]^{-}$.

This and other gallous salts, e.g. $GaAlBr_4$, $GaAlCl_4$, are soluble in benzene. It has been shown by Rundle and Corbett (57) that benzene solutions of gallium dichloride are very similar to those of silver perchlorate in the same solvent. Warf (33) showed that thallous perchlorate and tetrafluoroborate, however, were insoluble in toluene and Sharp (4) obtained similar results for hexa-fluoro-phosphate, - arsenate and-fluoroselenite.

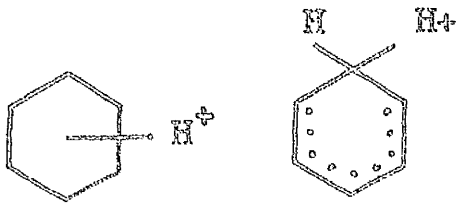
On the other hand, thallous trifluoroacetate is soluble in benzene (25), m-xylene, toluene and mesitylene (4). However it is almost certain that thallous trifluoroacetate is a covalent compound, since it melts at 120°C and sublimes at 160°C/1.5 mm. (25).

The mercury halides also dissolve in aromatic hydrocarbons. Other inorganic halides which form complexes with aromatic hydrocarbons include arsenic and antimony trichlorides, stannic chloride, phosphorus, tantalum, niobium and antimony pentachlorides and tungsten hexafluoride.

Separation techniques for the xylenes and for the methyl benzenes using liquid hydrogen fluoride/boron trifluoride mixtures (58) have been explained by postulation of a protonated aromatic nucleus (59). Two forms which arise, if this is the case, are:-

(a) by attachment of the proton to the benzene π electron system, and

(b) by the formation of a σ bond between the proton and the ring system.



(a) (b)

Olah et al. (60) have isolated complexes of the type $ArH^{+}BF_4^{-}$.

From partition studies, Winstein and Lucas (61) concluded that there is no complex formation between aromatic hydrocarbons and some metal ions in aqueous solution. Ions listed include cobalt (11), copper (11), zinc (11), nickel (11), chromium (111) and iron (111). The fact that carbonyls, cyclopentadienylides and complex acetylides of some of these metals can be obtained readily supports the argument that these ions are capable of interaction with π electron systems. This interaction of the d orbitals of the metal with the π system contributes largely to the stability of the complexes. In aqueous solution, however, there is competition for the metal ion between the aromatic system and water.

Since water is regarded as a good ligand, it is hardly surprising that aromatic hydrocarbon complexes are not formed under these conditions.

2. Ether

As mentioned previously, non-aqueous solvents containing atoms having an unshared pair of electrons possess remarkable solvent properties in spite of the fact that their dielectric constants are low. The solubility of many salts in ether and the formation of etherates is well-known.

The covalent compounds, mercuric chloride and bromide, dissolve in ether and the corresponding magnesium salts form etherates of the formula $MgX_2 . 2Et_2O$. Swarts (25) demonstrated the solubility of thallous, cupric and mercuric trifluoroacetates in ether and Sidgwick (36) lists many compounds which dissolve in ether and form etherates. The donor properties of this solvent have thus been well established.

Auto-ionisation of ether was proposed by Jander and Kraffczyk (62) to account for the conductivity of a series of ionic and covalent compounds in ether. The behaviour of lithium aluminium hydride in ether has been explained on this basis (62, 63).

Evans and Lee (64) showed that ether solutions of Grignard reagents conduct electricity, thus demonstrating the presence of ions even in solvents of low dielectric constant. Whatever entities are present in solution, it must be considered that the solubility of salts in ether is due to solvation of the ions by the ether. This is effected by co-ordination from one of the lone pair electrons on the oxygen atom of the ether.

Silver salts are somewhat unique in that, apart from chelates, few complexes, containing a metal-oxygen bond, exist. Notable examples of this type of bonding are the complexes of the fluoroacids and the perchlorate. Sharpe (5) demonstrated the solubility of silver tetrafluoroborate in ether, and a series of fluoroacid salts of silver was shown to be soluble in this solvent (4). The salts include silver hexafluoro-phosphate, - arsenate, - tantalate, - antimonate and - niobate. By displacement of the silver with copper powder, solutions of cuprous tetrafluoroborate and hexafluorophosphate were obtained. Moss (38) prepared silver hexafluoro-silicate and hexafluorotitanate and found that these too were soluble in ether.

Rare-earth tetrafluoroborates have been prepared by reacting the fluorides with boron trifluoride etherate (65).

Schwarzenbach has reported that a solution of nickel perchlorate can be obtained by neutralising a suspension of nickel ammonium perchlorate in ether with anhydrous perchloric acid (66). Lead perchlorate has been reported (67) soluble in many organic solvents although ether is not specifically mentioned.

3. Nitromethane

The presence of an atom containing unshared pairs of electrons and co-ordinating ability, described for ether, are also found in nitromethane. This, coupled with its relatively high dielectric constant ($\sim$36) should make it a remarkably good solvent. Only a few authors report its use as a medium for inorganic reactions. Olah and Quinn (68) report the preparation of silver tetrafluoroborate by passing boron trifluoride through a suspension of silver fluoride in nitromethane.

One of the most popular uses of this solvent is in the measurement of the conductivities of inorganic complexes. A number of authors (69, 70, 71) have reported the use of nitromethane in the determination of the number of ions present in compounds containing very large cations e.g. triphenyl methylarsonium, tetraethylammonium and di-(O-phenylenebisdimethylarsine) nickel (II), $[(C_{20}H_{32}As_4)Ni]^{++}$.

While much use of nitromethane has been made in conductivity work as mentioned above, it has also been used for the measurement of electronic absorption spectra in solution. Little has been published, however, on the co-ordination properties of nitromethane. Dunn and Buffagni (72), studied the nature of the complex - solvent interaction in the case of the triphenylmethylarsonium cation and some tetrahedral halogeno anions, e.g. $NiCl_4^{2-}$, $CoCl_4^{2-}$. They found evidence for strong interaction, resulting in octahedral species in solution.

It may be that the popularity of nitromethane will increase now that it has become commercially available in large quantities.

In the present work, solutions of perchlorates, trifluoroacetates and tetrafluoroborates of the first-row transition metals have been prepared in ether, benzene and nitromethane. These solutions were prepared by reacting a solution of the appropriate anhydrous silver salt with excess metal halide or metal, or stoichiometric quantities of each salt when the halide was soluble. The following table summarises the results. Reactions occurred in all cases. Where a metal entered into solution, the symbol (+) is used: solutions containing no metal are indicated (-).

Solutions as first prepared

		Ti^{3+}	V^{3+}	Cr^{3+}	Cr^{2+}	Mn^{2+}	Fe^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
ClO_4^-	E	+	+	+		+	+	+	+	+	+	+
	B	+	+	(+)	−	+	+	+	≈	≈	(+)	+
	N	+	+	+	≈	+	+	+	+	+	+	+
$O_2C.CF_3^-$	E	+	+	+		+	+	+	+	+	+	+
	B	+	+	+	≈	+	+	+	≈	≈	+	+
	N	+	+	+	≈	+	+	+	+	+	+	+
BF_4^-	E	+	+	+		+	−	+	+	+	+	+
	B	+	+	+	−	+	−	+	≈	≈	≈	+
	N	+	+	+	≈	+	≈	+	+	+	+	+

E = Ether
B = Benzene
N = Nitromethane

Explanation of the table is given by considering each metal separately.

A. Divalent metal ions

1. Copper (ii)

The most interesting feature of the solutions of copper (ii) salts (and also of cobalt (ii) and nickel (ii)) was the discovery of a new type of compound. This was first observed in the copper (ii) solutions. On the addition of anhydrous copper (ii) chloride to the silver salt in solution, an immediate colouration was observed. This was blue or blue-green in ether and benzene, and green with nitromethane. On prolonged shaking, the colour changed markedly becoming green in the first two solvents and yellow-green in the last named. This colour change was investigated by U.V. Spectroscopy and conductivity, and analysis in the case of the trifluoroacetate. The findings resulting from these investigations are reported in Chapter II. The conclusion which was drawn from the results is that two species can exist in solution (75) and, at least for the trifluoro-acetate, in the solid state. No analytical data could be obtained for the solid perchlorates or tetrafluoroborates. The two forms present in solution correspond to the formulae:-

$$\underset{(I)}{Cu(Cl)X} \text{ and } \underset{(II)}{CuX_2}$$

where X represents the strong acid anion. (I) may be converted to (II) by titrating the solution, first obtained, with silver salt dissolved in the appropriate solvent. The reactions may be formulated as:-

$$CuCl_2 + AgX \xrightarrow{\text{Excess Halide}} Cu(Cl)X + AgCl$$

$$Cu(Cl)X \xrightarrow{\text{Excess AgX}} CuX_2 + (2)AgCl$$

$$Cu(Cl)X + AgX \longrightarrow CuX_2 + (2)AgCl$$

There are obvious combinations possible because of these reactions. A solution of cupric chloro-perchlorate was titrated with silver trifluoroacetate. A precipitate of silver chloride was obtained but the solution obtained was very similar to that produced when the appropriate silver salt was used. Thus while it might be suggested that a compound of the formula $Cu(ClO_4)O_2C.CF_3$ is formed in solution, there is at present no analytical evidence to support the proposal.

From the weights of silver chloride precipitated, it was found that, within experimental error, only the chloro-compounds existed in the solutions as prepared. On titration with silver salt, a colour change was observed in all the solutions except the tetrafluoroborate in ether. In this case, the solution became colourless and a light-blue/green precipitate was formed together with the expected silver chloride. Analysis of the mixture showed that the blue-green compound was cupric bistetrafluoroborate, $Cu(BF_4)_2$.

The benzene solution of this anion was colourless. However, no silver was present in the solution and therefore reaction had occurred. A similar result was obtained when a large excess of silver tetrafluoroborate was added to cupric chloride, the solution being colourless. It must be concluded that neither form is soluble. When the benzene was removed from the first-mentioned solution by filtration and the residue dried by pumping under vacuum, treatment of this residue with nitromethane resulted in a yellow-green solution which was identical spectroscopically to the corresponding solution obtained directly from nitromethane.

The perchlorate solution in benzene decomposed rapidly after filtration to give an unidentified black substance and a clear solution. The solvent system was analysed by vapour-phase chromatography and found to contain only benzene. This black substance appeared in all perchlorate/benzene solutions although in some cases only after long standing.

2. Cobalt (II), Nickel (II)

Solutions of these ions were similar in their properties (except colour) and are discussed together.

No colouration was observed in cobalt or nickel solutions in benzene. Once again silver was absent from solution and washing the dried residue with nitromethane produced results similar to those obtained with copper.

Chloro-species were found to be present, but not exclusively, in the nitromethane and ether solutions as first prepared. It would appear that compounds of the formulae $M(CH_3)X$ and MX_2 (where X is the strong acid anion) exist as an equilibrium mixture.

The bis-compound, (MX_2), can be obtained in solution as for copper. Only in the case of the tetrafluoroborate in ether does the chloro-compound exist alone in solution. Addition of silver tetrafluoroborate gives results similar to those obtained for copper. A pale blue solid is precipitated from the cobalt solution and a light green solid from nickel. Again analysis showed these to correspond to the formulae $Co(BF_4)_2$ and $Ni(BF_4)_2$ respectively.

3. Manganese (II)

It was found that anhydrous manganese (II) chloride prepared from the hydrate would not react with silver salts. Reaction times of up to one month did not produce manganese in solution. Manganese metal was powdered to pass a 240 B.S. Sieve by using a percussion mortar. Reaction took place at a slow rate and two months' shaking was required to remove all the silver from solution. Unfortunately the solutions obtained contained little manganese except in the case of the trifluoroacetate in nitromethane. This made U.V. Spectra difficult to measure. From analysis of the solutions, however,

it would appear that all three strong acid salts were soluble to some extent in ether. Benzene solutions were extremely weak, oxidation to permanganate, during analysis, resulting in only a very pale pink colour. By far the strongest solutions were obtained in nitromethane.

4. Zinc (II)

Zinc solutions were prepared by reacting stoichiometric quantities of anhydrous zinc chloride and silver salt. In no case was a chloro-compound formed. The precipitated silver chloride corresponded to the calculated weight required for formation of the bis-compound in all cases.

5. Chromium (II)

Chromous salts react with ether (76) and no attempts were made to prepare solutions in this solvent. Solutions could not be prepared in benzene or nitromethane, silver precipitating in each case.

6. Iron (11)

In order to avoid oxidation to the ferric state, solutions of this ion were made up in an atmosphere of oxygen-free nitrogen. Metal entered solution in all cases. From the colours of the solutions obtained, it would appear that oxidation had taken place on standing. The tetrafluoroborate in ether decolourised slowly with the formation of a white precipitate [see iron (111)]. Chloride was found present in all solutions but, because of the presence of iron (111), no estimate of the species in solution could be made.

B. Trivalent metal ions

1. Iron (111)

These solutions were prepared from stoichiometric quantities as for zinc. The calculated weights of silver chloride were obtained for perchlorates and trifluoroacetates. No tetrafluoroborate solution could be prepared, immediate decomposition occurring. A dense white precipitate formed, much in excess of the weight calculated for silver chloride, and white fumes appeared in the reaction flask. It seems likely that ferric fluoride is formed as a result of the decomposition

of the tetrafluoroborate.

$$2Fe(BF_4)_3 \Rightarrow Fe_2F_6 + 6\,BF_3 \text{ (solvated)}.$$

2. Chromium (111)

It was found that chromium (111) solutions were difficult to prepare. Anhydrous chromium (111) chloride appears to have two forms, one 'active' and the other 'inactive'. The latter results from the dehydration of the hydrate using thionyl chloride. The 'active' form can be produced by heating chromium in a stream of dry chlorine at as low a temperature as possible for reaction to occur. The activity of this form may be due to traces of Cr^{2+} which can arise from the reactions:-

$$2CrCl_3 \rightarrow 2CrCl_2 + Cl_2$$

or $$Cr + Cl_2 \Longrightarrow CrCl_2$$

All solutions obtained for chromium (111) were coloured. No chloro-compounds were found to exist. The tetrafluoroborate solutions in ether and benzene were weakly coloured green. The perchlorate decomposed after filtration.

3. Vanadium (III)

All solutions prepared for this ion were coloured. Vanadium trichloride appears to be appreciably soluble in ether and nitromethane and thus solutions in these solvents were made from stoichiometric quantities. Vanadium trifluoroacetate could not be prepared in a pure state by removal of solvent from nitromethane solution. No chloro-compounds are formed.

4. Titanium (III)

All work involving this ion was carried out in a dry, oxygen-free atmosphere. Reaction occurred in all cases although attempts to obtain pure titanium (III) trifluoroacetate were unsuccessful. Chloro-species are absent from solution.

Solubilities

No accurate determination of solubilities was carried out. The strength of the solutions prepared was of the order of 5% W/V. A qualitative assessment of relative solubility showed the order BF_4^- < ClO_4^- < $O_2C.CF_3^-$ for the salts and benzene < ether < nitromethane for the solvents. All the solutions could be concentrated to some extent by removal of solvent under vacuum.

Experimental

All the solutions prepared were made up in a dry-box using anhydrous solvents and salts. The solutions were prepared in 100 ml. flasks and the ground glass stoppers sealed in the flasks using P.T.F.E. sleeves. As an added precaution the stoppers were wired on to the flask. Shaking was carried out on a mechanical shaker, reaction being completed in times varying from a few days to two months. The solutions were filtered in the dry-box using a sintered funnel (porosity 4) and a hand bulb connected to a Buchner flask. In many cases, repeated filtration was required and in some instances where separation was impossible by filtration, solutions were obtained by decantation. Starting materials were stored in the dry-box before use.

Preparation of Starting Materials

Solvents

Ether and benzene were dried over sodium wire and stored over molecular sieves. Nitromethane was dried over and then distilled onto molecular sieves. All solvents were stored in the dry-box which was kept free from moisture by means of open trays of phosphorus pentoxide.

Anhydrous Silver Salts

Silver perchlorate

The anhydrous salt was purchased from B.D.H. and was further dehydrated by continuous pumping at 50°C. The silver perchlorate was then left under vacuum over phosphorus pentoxide in the dry-box.

Silver Tetrafluoroborate

The preparation of Sharpe (5) was used. Dry silver borate was prepared by precipitation from silver nitrate and boric acid. The borate (1.5g) was placed in a silica bottle fitted with a standard B14 cone. Bromine (5ml.) was added to act as a moderator in the reaction. Bromine trifluoride was added, drop by drop, through a copper funnel. When excess had been added, the bromine and remaining bromine trifluoride were removed under vacuum on a normal vacuum line using a silica trap. The last traces of bromine trifluoride were removed by heating at 130° in vacuo for two hours.

Calculated for $AgBF_4$	: Ag	55.3%
Found	: Ag	54.6%.

Silver Trifluoroacetate

Anhydrous trifluoroacetic acid was added to an excess of silver carbonate wetted by a little water in a platinum dish. The solution was warmed on a steam-bath to ensure complete reaction and then filtered. The white solid obtained on evaporating the solution on a steam-bath was dried in vacuo over phosphorus pentoxide. The silver compound was then extracted with anhydrous ether and recrystallised from anhydrous ether.

Calculated for Ag OOC.CF_3	Ag :	48.9%.
Found	Ag :	48.2%.

Silver Hexafluoroantimonate

Silver hexafluoroantimonate was prepared by treating calculated quantities of silver metal and antimonious oxide with bromine trifluoride (59, 74). The product was heated at 130°C for two hours to remove the last traces of bromine trifluoride.

Calculated for $AgSbF_6$	: Ag	31.4%.
Found	: Ag	31.8%.

Anhydrous Metal Halides

Chromium (111) Chloride

Chromium(111) chloride was prepared by heating powdered chromium metal in a stream of dry chlorine. Two forms of this chloride exist. In order to obtain the 'active' form it was found necessary to chlorinate at the lowest temperature possible. The 'active' form gave chromium (111) solutions in the organic solvents.

Dehydration of the hydrate using freshly distilled thionyl chloride was also attempted. (75). This method, however, gave the 'inactive' form.

Calculated for $CrCl_3$: Cr 32.8%, Cl 67.2%.

Found : Cr 33.0%, Cl 67.6%.

Chromium (11) Chloride

Chromium (11) chloride was prepared by passing dry hydrogen chloride over powdered chromium metal at 1000°C. A white product, very sensitive to moisture was obtained.

Calculated for $CrCl_2$: Cl 57.8%.

Found : Cl 56.9%.

Cobalt (11) Chloride

Cobalt (11) chloride was prepared by partial dehydration of the hexa-hydrate under vacuum at 100°C. The product was then treated with freshly distilled thionyl chloride. When reaction ceased, the thionyl chloride was distilled off under partial vacuum using a dry nitrogen bleed. The product was washed several times with dry carbon disulphide and finally heated at 100°C under vacuum to remove the remaining carbon disulphide. A pale blue powder was obtained.

Calculated for $CoCl_2$: Co 45.4%, Cl 54.6%.

Found : Co 45.9%, Cl 55.0%.

Copper (11) Chloride

Copper (11) chloride was prepared from the dihydrate as for cobalt chloride. A yellow-brown powder was obtained.

Calculated for $CuCl_2$: Cu 47.3%, Cl 52.7%.

Found : Cu 48.0%, Cl 52.3%.

Manganese (11) Chloride

It was found that manganese (11) chloride prepared from the hydrate would not react with silver salts to produce solutions containing manganese. Manganese metal was used, powdering being effected by a percussion mortar.

Nickel (11) Chloride

Nickel (11) chloride was prepared from the hexa-hydrate as for cobalt chloride. A yellow powder was produced.

Calculated for $NiCl_2$: Ni 45.3%, Cl 54.7%.

Found : Ni 45.1%, Cl 54.0%.

Titanium (111) Chloride

Titanium (111) Chloride was donated by Laporte Titanium Ltd. and had been prepared by reduction of the tetrachloride by hydrogen at 900°C. All manipulations involving this compound were carried out under dry nitrogen. The stoppers of all flasks containing solution experiments of this chloride were sealed with wax as an added safeguard in preventing oxygen and moisture entering the reaction flask.

Vanadium (111) Chloride

Two methods were used to prepare this chloride. (a)Vanadium metal (5g) was placed in a silica tube tilted at an angle. The bottom end was connected by means of a ground glass joint to a flask containing sulphur monochloride. A stream of dry

carbon tetrachloride and oxygen-free nitrogen was passed over the metal at 660°C. Vanadium tetrachloride was formed rapidly and was carried over as a dark red vapour into the receiving flask which was cooled in ice-water. At the end of the reaction, tetrachloride left on the walls of the tube was warmed gently and the liquid readily ran into the flask. A reflux condenser fitted with a guard tube was then fitted and the mixture refluxed for 18 hours. Excess sulphur monochloride and reaction product, sulphur dichloride, were distilled off under reduced pressure. The purple solid remaining was washed repeatedly with anhydrous carbon disulphide in the dry-box and then heated under vacuum for 2 hours.

Calculated for VCl_3 : Cl 67.60%.

Found : Cl 67.34%.

(b) Vanadyl chloride penta-hydrate was prepared by gently boiling vanadium pentoxide in concentrated hydrochloric acid for one hour (36) then evaporating to small bulk. After cooling, methanol was slowly added to the deep blue solution and evaporation to small bulk repeated. Further treatment with methanol followed by evaporation resulted in the separation of a dark blue, non-crystalline mass.

Calculated for $VOCl_2 \cdot 5H_2O$: Cl 30.2%.

Found : Cl 28.7%.

The low chloride content may be due to co-ordination of some methanol to the vanadyl ion.

The blue material was refluxed with excess of freshly distilled thionyl chloride for two hours. The bulk of the thionyl chloride was then distilled off, 20-30 ml. fresh thionyl chloride added and the mixture refluxed for a further hour. A purple residue was obtained. The thionyl chloride was coloured orange-brown which may have been due to dissolved vanadium oxytrichloride. The thionyl chloride was then distilled off and the residue washed repeatedly with dry carbon disulphide. The purple product was dried by continuous pumping and stored under vacuum over phosphorus pentoxide and sodium hydroxide.

Calculated for VCl_3 : Cl 67.6%.

Found : Cl 67.3%.

Zinc (11) Chloride

Zinc (11) chloride was prepared from the hydrate as for the preparation of cobalt chloride. This material was used immediately after preparation.

Calculated for $ZnCl_2$: Cl 52.1%

Found : Cl 51.8%.

Iron (111) Chloride

Iron (111) chloride was prepared by passing a stream of dry chlorine over heated iron wire (77). The volatile product was collected in a trap and sublimed twice in an atmosphere of chlorine. Excess chlorine was then removed under vacuum. Dark crystals were obtained.

Calculated for $FeCl_3$: Fe 34.4%, Cl 65.6%

Found : Fe 34.7%, Cl 65.0%.

Iron (11) Chloride

This compound was prepared from anhydrous iron (111) chloride by heating with chlorobenzene at 130°C (78). The solid obtained was filtered, washed repeatedly with benzene and finally dried in vacuo.

Calculated for $FeCl_2$, Fe : 44.1%, Cl 55.9%

Found Fe : 43.7%, Cl 55.6%.

The absence of hydroxyl peaks in the near infra-red was taken to mean that anhydrous starting materials had been obtained.

CHAPTER II

Properties of Solutions and Solids

1. Absorption Spectra

One of the most important methods of examining transition metal compounds is by means of their ultra-violet and visible absorption spectra. In recent years the introduction of the reflectance spectrophotometer has added much information on solid materials, thus supplementing the already vast and still growing data obtained for solutions.

Accompanying and, in many ways promoting, the surge of interest, has been the increase in under-standing experimental observations as a direct result of theoretical advances. The literature published on the theory of d-d transitions and the resulting spectra is now vast. Books by Jørgensen (79) and Ballhausen (80) and a review by Dunn (81) cover most aspects.

Three main theoretical approaches to the problems of structure and spectra have been established up to the present time. Each method has its uses and also its limitations.

(a) Valence bond theory

This theory was proposed by Pauling (82) and enjoyed great popularity for many years. It is, unfortunately, of little use in the interpretation of spectra. This arises from the lack of provision for excited states and the energy levels associated with them.

(b) Crystal Field theory (Electrostatic)

This approach was first used by Penney and Schlapp (83) to investigate apparent discrepancies in magnetic properties of crystals, thought to be due to crystal forces. The assignment of absorption bands of low extinction coefficient arising in the visible and ultraviolet regions has been dealt with very efficiently by means of this method. Such bands have been related to definite transitions in the case of octahedral and tetrahedral complexes and their associated distorted forms.

(c) Ligand Field theory

The ligand field theory uses the basic electrostatic approach but in addition takes into consideration the molecular orbital concept. As such it is probably the superior method for dealing with transition metal complexes. This 'hybridisation' of the above theories is most successful for complexes where strong interaction between the ion and ligand orbitals occurs.

The transitions involve either charge transfer (84) or orbitals which are largely delocalised over the central metal ion and the ligands.

In order to calculate atomic energy levels in a polyelectronic system, the forces acting within the atom are considered in order of magnitude. The final levels are reached by a series of approximations starting with the largest forces. For a polyelectron atom or ion, three main types of force exist:

(a) Central field forces

(b) inter-electronic repulsion forces

(c) spin-orbit coupling forces.

Force (a) is by far the largest since this condition is necessary for a stable atom. It is a coulombic force, involving attraction between a central positive nucleus and the electrons. Forces (b) and (c) are also important. If $b >> c$, the levels resulting are said to belong to the Russell-Saunders coupling scheme or (LS scheme). If, on the other hand, $c >> b$ then the final levels are ascribed to the jj scheme. This latter scheme is applied generally to heavy atoms where $Z \gtrsim 80$.

The Russell-Saunders scheme has been well established for atoms with $Z \lesssim 30$ and this includes the first row transition elements. The one electron atom scheme is prepared and the interelectronic repulsion effect on this configuration found. The previously degenerate configuration is thereby split into groups of levels of lower degeneracy known as terms. These terms are specified by the total atomic orbital angular momentum (L) and by the spin angular momentum (S).

$$L = \sum_i l_i = \begin{array}{ccccccc} 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ S & P & D & F & G & H & I \end{array}$$

and $S = \sum_i s_i$ where S has multiplicity $r = 2S + 1$.
Thus the term is denoted $^r L$.

When L and S are non-zero, magnetic fields are generated and hence orientation occurs so that the interaction energy between the two fields is at a minimum. The coupling or interaction gives rise to the quantum number J which is a measure of the total angular momentum of the atom including contribution from the spin and orbital momenta. J has values

$$J = L + S,\ L + S - 1, \ldots\ldots\ L - S.$$

The term is therefore now denoted $^r L_J$, e.g. for chromium (111):

$S = 1\frac{1}{2}, L = 3, J = {}^{9}/_{2}, {}^{7}/_{2}, {}^{5}/_{2}, {}^{3}/_{2}$.

Ground term is ^4F.

The levels arising are:-

$$^4F_{9/2}, \ ^4F_{7/2}, \ ^4F_{5/2}, \ ^4F_{3/2}.$$

The term multiplet is applied to the values of J arising from the same term and each J value is known as a component.

Application of Hund's rules makes it possible to determine the ground energy level.

(i) Of the Russell-Saunders states arising from a given electronic configuration and permitted by the Pauli exclusion principle, the most stable state will be the one with the greatest multiplicity.

(ii) Of a group of terms with a given S value, the term with the largest L value has the lowest energy.

(iii) Of the states with given L and S values in a configuration consisting of less than half the electrons in a sub-group, the state with the smallest J value is normally the most stable. The converse holds for a configuration with more than half the electrons in a sub-group.

In the crystal field theory, the effect of electric fields of various symmetries on the field free atomic terms and degenerate orbitals is considered.

Three types of energy are relevant if Russell-Saunders coupling is assumed.

(i) crystal field energy

(ii) spin-orbit coupling energy

(iii) energy distance between terms of the same configuration.

In all cases, (ii) must be less than (iii) and so three orders may arise.

(a) (i) < (ii) < (iii).

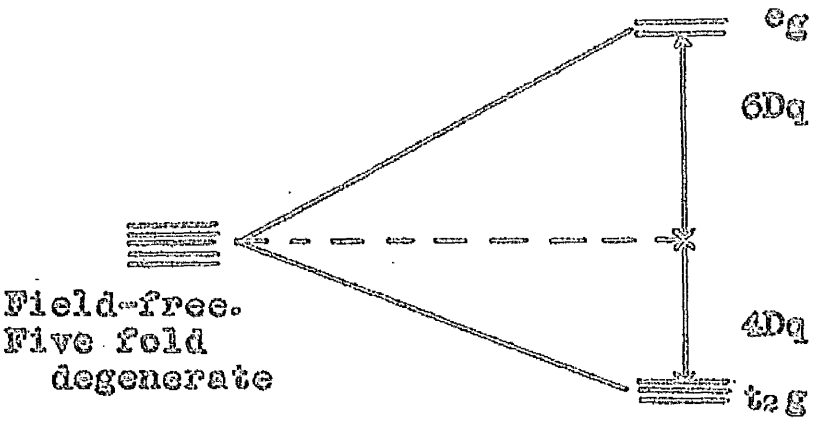
(b) (ii) < (i) < (iii).

(c) (ii) < (iii) < (i).

Cases (a) and (b) are known as weak-field limits and (c) as the strong field limit. Case (b) applies for d electrons of the first-row transition series. This means that the energy distance between terms from the d^n configuration is large enough so that crystal field effects do not cause interaction.

The simplest case is the d^1 configuration. The only term arising here is ^2D and this has the components $^2D_{3/2}$ and $^2D_{5/2}$. Titanium (III) has such a configuration. When the tripositive titanium ion is surrounded by six ligands, e.g. water, octahedrally placed in relation to it, the previously five-fold degenerate D term splits into two new levels,

one threefold degenerate, t_{2g}, and one doubly degenerate, e_g. These levels are separated by an energy difference of $\triangle$ or 10Dq. It can be shown by calculation that the triply degenerate level lies at 4Dq below the original unperturbed d level and that the doubly degenerate level lies at 6Dq above the original. The effect is shown in diagram:



It is obvious that the single d electron occupies a t_{2g} orbital and also that an electronic transition will occur when the d electron is transferred to an e_g orbital. This will occur at a wavelength or frequency corresponding to the separation 10Dq (or $\triangle$) between the two types of orbital. The band which results has a maximum at 490 mu (20,300 cm^{-1}) for the $Ti(H_2O)_6^{3+}$ ion,

(85) which gives a Dq value of 2050cm^{-1}.

The band described above is 'weak' in that the extinction coefficient, ε, is small (~ 5). This is a feature of the so-called d-d transitions for first row transition elements.

Theoretical explanations of the low intensities of such transitions are based on selection rules which determine to what extent the transition is 'allowed'.

In a free atom any transition which results in a change in the number of unpaired electron spins is said to be multiplicity forbidden and, at best, can appear only very weakly in absorption. A second, and more important rule is that transitions which involve redistribution of electrons in the same quantum shell are 'forbidden'. Thus transitions between the different states of a d^n configuration should not be observed. This is a case of the Laporte selection rules. However, the rule does not hold completely when we consider the metal ion forms part of a compound.

Some mechanisms have been proposed to explain these transitions (86). Whatever the true answer is, there remains the fact that the transitions are weakly allowed with ε values ranging $0-10^2$. In spin-allowed transitions, which occur at much shorter wavelengths, εvalues are of the order 10^3 upwards.

The strong field limit (case C) implies that the energy gap between the t_{2g} and e_g levels may become so large that interaction between states arising from configurations involving both t_{2g} and e_g may be ignored. This does not allow a full explanation of all the features of a spectrum in the strongly perturbing field limit. Consideration must be given, by comparison with an intermediate field, to some $t_{2g} - e_g$ interaction In a field free atom or ion or in a weak field case, the maximum multiplicity is six whereas in a strong field case the maximum multiplicity is four. Cobalt (III) provides an example of this effect. In a weak field the complexes have magnetic moments $\sim$ 5.4 B.M. corresponding to four unpaired spins whereas in strong fields they become diamagnetic. Since the present work is concerned with weak-field complexes, no further discussion on the strong field case is necessary.

The Spectra of First-Row Transitional Metal Salts of some Strong Acids.

Any assignments of the bands observed and reported in this chapter are made by comparison with published spectra. For this comparison, full use has been made of the book by Jorgensen (79) and the review by Dunn (81). A mathematical explanation is outwith the scope of this project. The metal ions of d^n configuration are considered in increasing magnitude of n. Extinction coefficients, ε max., have been calculated for the observed maxima. It is not possible to calculate extinction coefficients for bands obtained by measurement of reflectance spectra. Relative intensities are indicated by the usual abbreviations. (vs = very strong, s = strong, m = medium, br = broad.)

Note: In many spectra, it has been found that the charge-transfer bands make observation of short wavelength d-d transitions difficult or impossible to record. Figures are quoted in $cm^{-1} \times 10^{-3}$.

d^1

The metal ion studied was Titanium (111). The published spectra on the $Ti(H_2O)_6^{3+}$ ion is fairly extensive.

Interest in the spectra is obviously due to the fact that only one transition occurs, as previously discussed. However, the band is not symmetrical and a shoulder has been observed (87, 88). This is explained as being due to a split excited e_g state, the split being caused by a Jahn-Teller distortion. In the present work no shoulder was observed. This omission is presumably due to the large charge transfer bands which appeared close to the d-d transitions. Results are shown in Table I.

$\triangle$ values have been calculated for the ligands and are given in the following table. Units used are kK = $cm^{-1} \times 10^{3}$.

Ligand field splitting values ($\triangle$ or 10Dq)

Compound	Ether	Benzene	Nitromethane
ClO_4^-	20.3	20.8	20.9
$O_2C.CF_3^-$	20.3	21.2	21.3
BF_4^-	21.0	23.8	21.7

The $\triangle$ value quoted for $Ti(H_2O)_6^{3+}$ is 20.3 (85). The anions in ether and nitromethane show the order of field strength to be $ClO_4^- \leq O_2C.CF_3^- < BF_4^-$.

TABLE I

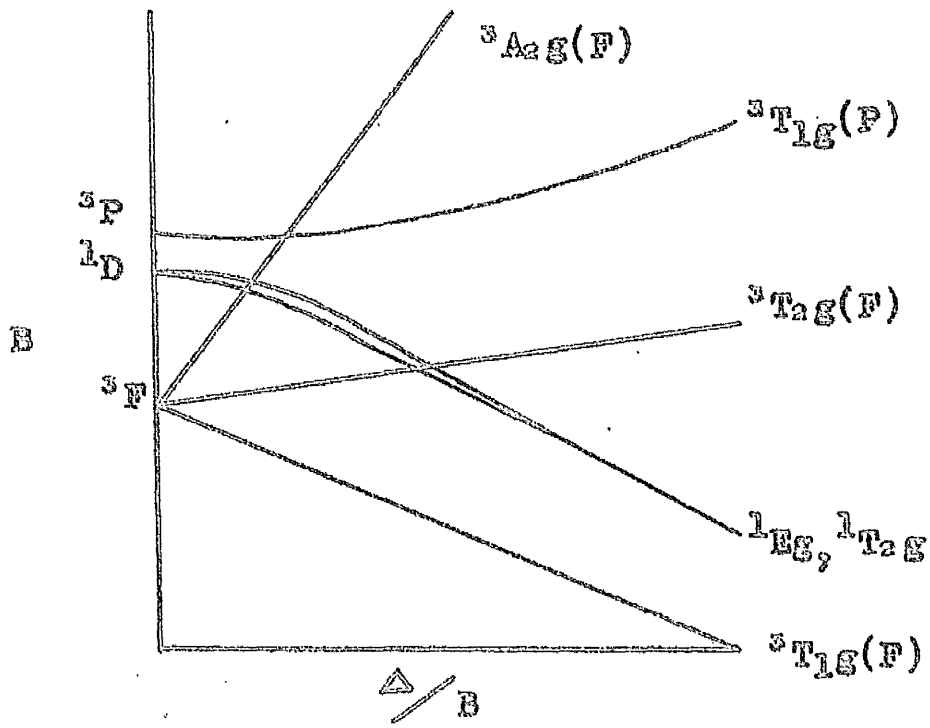
Titanium (III)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	40.5	-	31.3	-	24.4	-
	20.3	4.1	20.8	7.8	20.9	8.5
$O_2C.CF_3^-$	41.1	-	33.3	-	24.4	-
	20.3	7.1	21.2	10.2	21.3	7.6
BF_4^-	41.7	-	34.5	-	25.0	-
	21.0	3.7	23.8	12.4	21.7	8.8

This order is maintained in benzene but the large value of Δ found for benzene solutions is rather surprising. Since the ligand field strengths are similar to that of water, it would be reasonable to place the systems described near water in the spectrochemical series. Further evidence from Δ values is given later in this chapter.

d^2

For a d^2 complex, the following diagram (after Tanabe, Sugano) shows the energy levels arising in an octahedral field.



Both the hydrate and oxalato-complexes of tripositive vanadium show well defined transitions at $\sim 17,000 cm^{-1}$

and $\sim 24,000 cm^{-1}$. These have been assigned by a number of authors as $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$. Two low-lying singlet states ^1Eg and $^1T_{2g}$ also exist but no trace of these has been reported. Results are reported in Table II.

The charge transfer bands make difficult the task of detecting the maximum absorption $\sim 25,000 cm^{-1}$. Consequently, the ether solutions of the trisperchlorate and tristrifluoroacetate are the only examples showing the two expected absorptions. The peaks reported in nitromethane solutions $\sim 25,000 cm^{-1}$ may be due to d-d transitions but it is impossible to be definite on this point. A feature of all spectra in nitromethane is an intense peak in this region. It would appear that the d-d transition $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ and the charge transfer peak $\sim 25,000 cm^{-1}$ cannot be distinguished.

d^3

Chromium (III) has been extensively studied and many spectra published. The ground state is ^4A_2g and six excited levels have been identified.

TABLE II

Vanadium (III)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	40.8	875	35.7	480	24.7	770
	25.6	200				
	14.7	2.4	20.2	35	18.2	120
					9.8	48
$O_2C.CF_3^-$	40.0	1650	28.2	820	24.4	980
	23.8	190				
	16.1	11.0	20.8	125	20.3	137
	12.8	28.0	15.6	4.0		
BF_4^-	40.0	1200	31.3	920	25.0	1130
	12.5	12.5	20.4	150	17.5	24

^4A_2g -> ^2Eg ≈ 15,000cm^{-1} (ruby)

-> ^2T_1g ≈ 15,500cm^{-1} (ruby)

-> $^4T_2g(F)$ ≈ 17,400cm^{-1} (hydrate)

-> ^2T_2g ≈ 22,000cm^{-1} (ruby)

-> $^4T_1g(F)$ ≈ 24,700cm^{-1} (hydrate)

-> $^4T_1g(P)$ ≈ 37,000cm^{-1} (hydrate)

It is interesting to note that of these six observed transitions, three are multiplicity forbidden and should thus be weak or very weak in intensity. Band positions are quoted in Table III.

(a) The solution of chromium (111) triperchlorate in benzene decomposed as the spectrum was being measured. The positions of maxima quoted are therefore in some doubt.

(b) Solutions of the tristetrafluoroborate in ether and benzene were coloured green but were so weak as to make spectroscopic examination impossible. Concentration of the solutions by vacuum distillation caused some precipitation of solid material.

The spectra of the chromium (111) solutions show maxima which correspond closely to the transitions theoretically derived for the ion in an octahedral environment. Δ values have been calculated for the ligands and are reported later.

TABLE III

Chromium (III)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	40.0	3.1	33.3	11.5	26.7	0.25
	23.3	0.14	18.7	3.6	23.8	0.33
	16.0	0.1	17.2 (a)	0.58	17.1	0.33
	14.3	0.07	14.9	0.29	15.2	0.24
$O_2C.CF_3^-$	40.0	2.9	33.3	5.0	25.6	0.74
	23.3	0.86	22.2	1.2	23.3	0.79
	16.3	0.70	15.9	1.3	17.1	0.67
	14.5	0.25	14.4	0.33	14.9	0.31
HF_4^-	(b)		(b)		26.3	1.2
					22.2	0.84
					16.7	0.28
					14.7	0.12

Solid Trifluoroacetate (reflectance spectrum) 41.7(s), 32.3(m), 24.1(m), 17.4(m), 14.7(sh).

d^4

Chromium (II)

It was not possible to prepare any divalent chromium solutions. Chromous ion reacts with ether (09) and no metathetical preparations were attempted in that solvent. In benzene and nitromethane, decomposition occurred rapidly and silver was deposited.

d^5

Two d^5 ions have been studied. In both Iron (III) and Manganese (II) the bands which appear are very weak and in many cases not observed. The weakness of the bands can be explained by the fact that, in the weak field case, the transitions are all multiplicity - (or spin-) forbidden. In addition to this, large charge transfer bands mask these very weak transitions in some cases.

Manganese (II)

The spectra of complexes of this ion with many ligands have been extensively covered. For the hexa-hydrate the following assignments have been made (90).

$^6A_{1g}$ -> $^4T_{1g}$(G) $\sim$ 19,400cm^{-1}

-> $^4T_{2g}$(G) $\sim$ 22,800cm^{-1}

-> ^4Eg, $^4A_{1g}$(G) $\sim$ 25,200cm^{-1}

-> $^4T_{2g}$ (D) $\sim$ 28,200cm^{-1}

-> ^4Eg(D) $\sim$ 29,900cm^{-1}

-> $^4T_{1g}$(P) $\sim$ 35,000cm^{-1}

-> $^4A_{2g}$ (F) $\sim$ 40,700cm^{-1}

-> $^4T_{1g}$(F) $\sim$ 41,900cm^{-1}.

Since all transitions involved in a d^5 ion are spin-forbidden, it would be expected that the intensity of the bands would be extremely low. Results are listed in Table IV.

Solutions of manganese (II) complexes in benzene were extremely weak. Analysis of solutions showed that the strength was of the order of 0.2%. Again the nitromethane solutions, while being the most concentrated, showed charge transfer peaks which masked any d-d transition maxima. Ether solutions gave maxima $\sim$ 20,000cm^{-1} of very low extinction coefficient.

TABLE IV

Manganese (II)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	45.5	>5000	34.7	4890	24.6	>5000
	21.9	0.1				
	20.0	0.02				
$O_2C.CF_3^-$	45.8	>5000	35.1	3760	25.0	>5000
	25.5	0.01				
	21.9	0.02				
	20.0	0.09				
BF_4^-	46.5	> 5000	35.8	4180	25.0	> 5000
	24.5	0.09				
	21.8	0.03				
	19.8	0.03				

Iron (111)

The spectrum of the hexahydrate has been measured by several authors but characterisation has proved difficult and there are discrepancies between the published maxima. The first transition has been given as 12,600cm^{-1} (91) and 14,300cm^{-1} (92,93). The spectrum of Fe^{3+} in beryl where the ion is co-ordinated to six oxygens, has been investigated by Dvir and Low (94). Tentative assignments have been made as follows:-

$$^6A_{1g} \rightarrow {}^4T_{1g} \sim \begin{matrix} 12,300cm^{-1} \\ 14,200cm^{-1} \end{matrix}$$

$$\rightarrow {}^4T_{2g} \sim \begin{matrix} 17,500cm^{-1} \\ 20,000cm^{-1} \end{matrix}$$

$$\left.\begin{matrix} \rightarrow {}^4E_g \\ \rightarrow {}^4A_{1g} \end{matrix}\right\} \sim 23,000cm^{-1}$$

$$\rightarrow {}^4T_{1g} \sim 26,500cm^{-1}$$

The spectra of iron (111) solutions are given in Table V.

(a) The solution of iron (111) triperchlorate in benzene decomposed rapidly after filtration and it was not found possible to measure the spectrum.

TABLE V.

Iron (III)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	38.5	3500	(a)		24.7	1500
					17.5	250
	29.4	800			10.3	0.8
$O_2C.CF_3^-$	46.5) 38.3) 37.0)	5000	35.1	1650	25.6	5000
			29.0	1392	10.3	0.97
	18.5	27	(21.7)	125		
	10.8	0.8	(21.1)	53		
			18.5	27		
BF_4^-	a.		a		a	

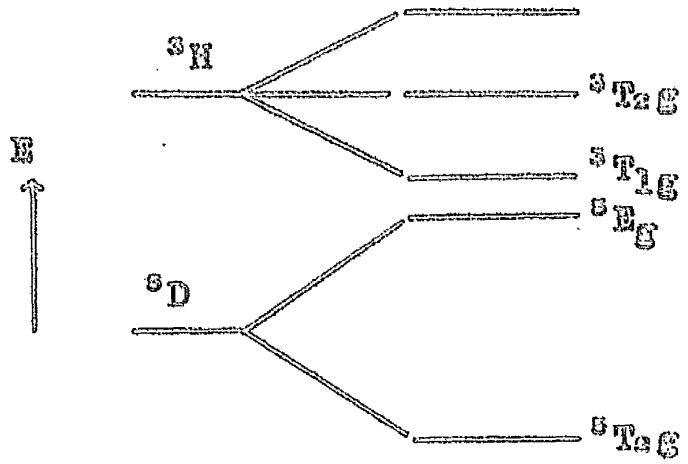
Solid Trifluoroacetate (Reflectance Spectrum) 21.8 (sh), 17.9 (sh) 33.8 (v.s.)

The spectra of iron (111) solutions should consist of a number of peaks of low intensity. Explanation of this effect has already been given in the case of manganese (11). The fact that some of the maxima observed have $\varepsilon_{max.}$ values which are fairly large can be accounted for by the close proximity of these peaks to the charge transfer bands. In some cases, the band appeared as a shoulder on the very intense charge transfer band. Since it was difficult to subtract the contribution of the charge transfer band to the optical density at the shoulder, the ε_{max} values for the d-d bands are tentative. The solid trifluoro-acetate showed two shoulders on the side of a very strong charge transfer band $\sim 35,300 cm^{-1}$.

d^5

Iron (11)

The electronic ground state is ^5D. The splitting scheme for a d^5 ion in a weak octahedral field is shown in the diagram.



In the absorption spectra of the pale green ion $Fe(H_2O)_6^{2+}$, a double peak has been observed at 10,000cm^{-1}. This is assigned as ^5T_2g -> $^5Eg(D)$ by several authors (95,96,97). The splitting is due to a Jahn-Teller effect in the excited state (98). A number of very small peaks have been reported but not fully assigned. These occur around 20,000cm^{-1} and are presumably ^5T_2g -> ^3T_1g, ^3T_2g etc. Results are quoted in Table VI. All the iron (ll) solutions contained varying quantities of iron (lll). In view of this fact, it is felt that $\varepsilon_{max.}$ values would have little significance as well as being almost impossible to calculate. The only significant feature of the spectra of the iron (ll) solutions is that they all show increasing absorption in the region 11,000-8,500cm^{-1}.

TABLE VI.

Iron (II)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	39.2	-	32.3	-	24.4	-
	≈ 9.1	-	≈10.0	-	≈ 8.5	-
$O_2C.CF_3^-$	39.2	-	34.5	-	24.7	-
	≈10.0	-9.1 -	≈10.0	-	≈ 8.7	-
BF_4^-	45.5	-	35.7	-	26.3	-
	≈10.0	-9.1 -	≈10.0	-9.1 -	≈ 9.5	-

The exact maximum for each peak was very difficult to measure since the band was very broad. The transition $^5T_2g \rightarrow {}^5Eg(D)$ is found in this region. No trace of the quintuplet-triplet transitions $\approx 20,000\ cm^{-1}$ was observed in the iron (II) solutions studied.

The solutions prepared by metathesis contained chloride ion. This was removed by addition of the appropriate silver salt. The values quoted in the table correspond to the chloride-free solutions. The solutions containing chloride ion differ little spectroscopically from the solutions for which spectra are reported. Any distinction between the two species in solution is rendered difficult by the breadth of the absorption bands resulting in indefinite maxima.

d^7

Cobalt (II)

The hexahydrate has been studied and the known transitions are:-

$^4T_{1g}$ -> $^4T_{2g}(F)$ ~ 8-9,000 cm^{-1}

-> ^2Eg ~ 11,000 cm^{-1}

-> $^4A_{2g}(F)$ ~ 16-18,000 cm^{-1}

-> $^4T_{1g}(P)$ ~ 20-21,000 cm^{-1}

Taking a Dq value of 970 cm^{-1}, (99), Orgel has predicted transitions at 8,100, 17,500 and 22,000 cm^{-1}. Experimentally a band has been observed ~ 19,600 cm^{-1} and this has been explained by considering this band to include both of the shorter wavelength quartet-quartet transitions as well as some quartet-doublet contribution. Cobalt (II) spectra are recorded in Tables VII and VIII.

Cobalt (II) chloro-perchlorate, -trifluoroacetate and -tetrafluoroborate solutions varied in colour from blue or violet to red. The corresponding bis-solutions were all red in colour. Cobalt (II) bistetrafluoroborate precipitated from ether solution on addition of silver tetrafluoroborate to the chloro-tetrafluoroborate.

TABLE VII

Cobalt (11) Chloro series (Co(Cl)X).

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	41.0	259	-	-	25.0	-
	40.0	208			21.3	4.6
	30.3	47			19.6	5.0
	18.2	12.9			7.69	1.0
	17.4	12.9			(7.14)	1.0
	16.1	11.0			5.26	0.5
	14.4	7.8				
	7.46	5.0				
$O_2C.CF_3^-$	41.7	20	-	-	25.2	-
	19.6	8.0			20.4	10.8
	17.5	9.5			17.4	20.1
	16.1	8.0			16.0	20.1
	14.7	6.5			14.7	20.5
	7.14	1.0			7.41	6.0
BF_4^-	41.3	71.3	-	-	25.1	-
	18.0	13.2			21.3	6.2
	17.4	13.2			19.2	6.5
	6.67	1.3			7.41	1.0
					5.24	1.0

Solid Trifluoroacetate 25.6(m), 20.0(sh), 18.2 (m).
(Reflectance Spectrum)

TABLE VIII.

Cobalt (II) Bis series (CoX_2)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	41.0	278	-		25.3	309
	20.0	11.0			18.5	16.5
	18.2	16.9				
$O_2C.CF_3^-$	41.6	140	-		25.0	417
	20.2	7.7			18.5	17.0
	17.8	7.9				
BF_4^-	Fpt		-		25.2	503
					20.0	7.0

Solid Trifluoroacetate ≈ 50.0(v.s.), 20.2(m), 18.7(m).
(Reflectance spectrum)

By comparison, the spectra of the solutions of CoX_2 (where X is the strong acid anion) were much more simple than those of the corresponding chloro-species, Co(Cl)X. The maxima in the range 10,000 - 5,000 cm^{-1} were not well defined. The spectra of cobalt (11) bisperchlorate, bistrifluoroacetate and bistetrafluoroborate in nitromethane show only one peak $\sim$ 18,000cm^{-1}. The disappearance of the less intense minor peak $\sim$ 20,000cm^{-1} may be due to the effect of the charge transfer bands appearing $\sim$25,000cm^{-1}. Ligand field strengths for the cobalt (11) complexes have been calculated and are reported later in this chapter.

d^8

Nickel (11)

Octahedral complexes of nickel (11) are very common and the spectra of these have been extensively examined. For octahedral nickel (11), three triplet-triplet transitions should be observed. In addition some triplet-singlet bands are possible, these being spin-forbidden.

Assignments which have been made are:-

^3A_2g -> $^3T_2g(F)$ ≈ 8,600 cm^{-1}

-> $^3T_1g(F)$ ≈ 13,500 cm^{-1}

-> $^1E_g(D)$ ≈ 15,400 cm^{-1}

-> $^1A_1g(G)$ ≈ 18,500 cm^{-1}

-> $^3T_1g(P)$ ≈ 25,500 cm^{-1}

Band positions are given in Tables IX and X.

The colours of solutions of salts of the formula NiX_2 were similar to those of the chloro-compounds Ni(Cl)X. As in the case of cobalt (II) bis-salts, the region 10,000 - 5,000cm^{-1} gave peaks, the position of which could not be accurately determined.

The spectra, in general, correspond to octahedrally complexes nickel (II). Ligand field values have been calculated and are reported later.

Nickel (II) bistetrafluoroborate precipitated from ether solution when the solution of the chlorotetrafluoroborate was quantitatively converted using silver tetrafluoroborate in ether.

TABLE IX.

Nickel (II) Chloro Series (Ni(Cl)X)

Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	23.5	23.1	-		25.0	12.9
	14.1	3.8			14.9	3.3
	12.5	6.8			13.7	3.4
	7.46	3.8			8.55	3.4
	6.02	2.7			6.90	2.7
	5.16	1.3			5.21	5.0
$O_2C.CF_3^-$	24.4	15.5	-		25.3	18.6
	14.6	4.5			14.9	4.7
	13.3	4.9			13.7	3.6
	8.48	4.9			8.62	5.2
	6.06	1.3			7.14	1.8
BF_4^-	24.1	13.3	-		25.6	34.0
	13.2	5.9			16.4	8.0
	8.5	2.8			9.17	8.0

Solid Trifluoroacetate 25.6(s), 14.9(m), 13.7 (m).
(Reflectance spectrum)

TABLE I.

Nickel Bis Series (NiL_2)

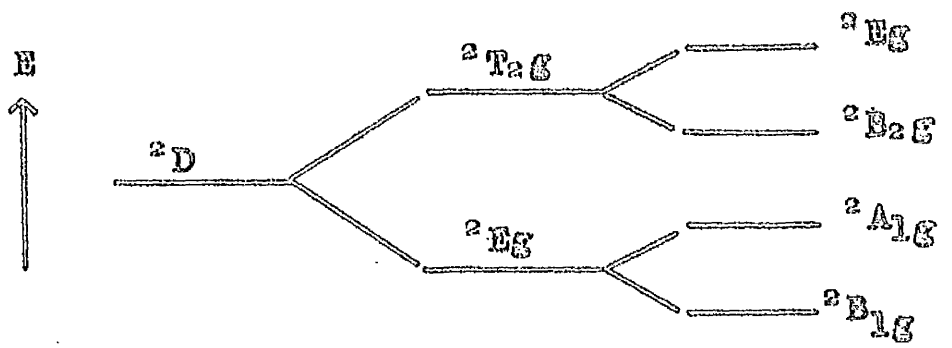
Solvent	Ether		Benzene		Nitromethane	
Sample	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
ClO_4^-	23.3	17.5	-		24.8	16.0
	14.2	6.0			14.8	4.7
	12.4	8.0			13.7	4.7
$O_2C.CF_3^-$	24.5	15.0	"		24.8	19.8
	14.6	7.2			14.8	4.4
	13.5	7.3			13.6	3.4
BF_4^-	ppt		-		25.3	28.5
					16.7	7.4

Solid Trifluoroacetate 47.6(vs), 25.0(s), 14.9(m), 13.5(m). (Reflectance Spectrum)

d^9

Copper (11)

The d^9 ion in a perfectly octahedral environment should show only one transition, i.e. $^2Eg \Rightarrow {}^2T_2g$. This, of course, means that the spectral behaviour of Cu(11) should be as found in Ti(111) complexes, with the level order inverted. However, the ^2Eg level is highly susceptible to John-Teller perturbation. It would therefore be expected that no perfectly octahedral copper (11) complex would exist, and this is in agreement with experimental evidence. Both levels split into two components as shown in diagram:



Thus three transitions are possible. In practice, the spectra of copper (11) complexes consist of a broad band. In the case of $Cu(H_2O)_6^{2+}$, this has a maximum at 12,600 cm^{-1} and almost certainly contains more than one transition.

Holmes and McClure (96) analysed the polarised absorption spectrum of $CuSO_4.5H_2O$ and found three transitions in the region 10,000-14,000cm^{-1}. The values found for copper (11) solutions are given in Tables XI and XII.

The spectra of all copper (11) solutions consisted of broad bands extending over $\sim$500cm^{-1}. The chloro-tetrafluoroborate in ether gave a spectrum in which some separation occurred ($\sim$ 100cm^{-1}). The corresponding chloro-hexafluoroantimonate in the same solvent showed similar splitting, maxima occurring at 11,000cm^{-1} and 12,350cm^{-1}. Both solutions gave precipitates when converted to the bistetrafluoroborate and bis-hexafluoroantimonate respectively using the appropriate silver salt.

d^{10}

Zinc (11)

As would be expected for a d^{10} ion, zinc (11) shows no d-d transitions. The spectral data collected for this ion in its complexes is limited to a recording of the bands which appear in the charge transfer region. These bands are listed in Table XIII.

TABLE XI.

Copper (II) Chloro Series (Cu(Cl)X)

Solvent	Ether		Benzene		Nitromethane	
Sample	λ max.	ε max.	λ max.	ε max.	λ max.	ε max.
ClO_4^-	44.4	1410	38.2	70	26.3	49.9
	36.9	2710	36.0	135.5		
	12.6	42.1	12.4	3.5	13.7	23.7
$O_2C.CF_3^-$	40.0	4000	35.8	1750	26.5	16.2
	12.5	135.4	12.5	58.2	13.8	70
BF_4^-	40.2	2840				
	39.2	3040				
	38.3	2980			26.5	796
	33.3	4810				
	11.6	495			14.3	139
	10.6	525				

Solid Trifluoroacetate $\sim$ 43.5(v.s.), 12.7 (br).
(Reflectance spectrum)

TABLE XII.

Copper (II) Bis Series (CuX_2)

Solvent	Ether		Benzene		Nitromethane	
Sample	λ max.	ε max.	λ max.	ε max.	λ max.	ε max.
ClO_4^-	44.5	1289	38.0	718	26.3	189
	13.2	55.6	14.3	14.0	14.5	39.2
$O_2C.CF_3^-$	41.0	3510	37.0	1930	26.4	214
	13.0	71.9	15.2	30.8	15.5	65.0
BF_4^-	Ppt		⇦		26.4	648
					15.6	81.0

Solid Trifluoroacetate 41.5 (vs.) 13.3 (br.)
(Reflectance spectrum).

TABLE XIII.

Zinc (II)

Solvent	Ether		Benzene		Nitromethane	
Sample	λ max.	ε max.	λ max.	ε max.	λ max.	ε max.
ClO_4^-	45.4	25.6	36.0	17.4	26.6	3.0
	40.3	3.2			23.6	1.4
	39.2	2.6				
	38.3	1.3				
$O_2C.CF_3^-$	45.0	19.0	36.0	15.6	27.1	2.9
	36.2	22.8			26.4	3.6
					26.1	3.1
					25.9	2.9
BF_4^-	44.2	109	37.0	49.1	26.4	31.2
	39.2	22.8	36.0	103.6	24.4	3.9
	38.5	11.4	29.0	13.1		
	35.7	5.7				

Ligand Field Calculations

Ligand Field Calculations

It is possible to calculate certain fundamental properties associated with the ligands surrounding the central metal atom in a complex.

(a) Δ or 10Dq

This is the orbital energy difference between the ground state and the first excited state. Essentially it is a measure of the extent to which the degenerate d orbitals are split by the influence of the ligand. Comparison of values of Δ leads to the spectrochemical series.

Δ is a complex quantity having contributions from various sources. Four of the important factors are:

(i) Electrostatic perturbation

(ii) Effect of ligand σ lone pairs

(iii) Metal -> ligand $d\pi$ - $P\pi$ bonding

(iv) Ligand -> metal $P\pi$ - $d\pi$ bonding.

Of these, (i), (ii) and (iii) increase Δ, while (iv) acts in the opposite direction. The first factor is less important than the remaining three.

(b) B

B is the symbol used for one of the Racah parameters. These inter-electronic repulsion parameters (A, B and C) are a measure of the separation

of terms and are related, in a definite manner, to the energy differences of certain terms.

The metals for which values were calculated were cobalt (11), d^7, nickel (11), d^8, and chromium (111), d^3. The relationship between B and the separation of the terms is given in the following table.

Ion	Terms	Separation
d^3, d^7	$^4F - {}^4P$	15 B
d^8	$^3F - {}^3P$	15 B

The separation of the terms can be found experimentally from electronic absorption spectra and hence the value of B calculated.

(c) β

This is the ratio of the value of B found experimentally to the corresponding B value calculated for the gaseous ion (B^1).

$$\beta = \frac{B}{B^1}$$

Having found the B value from observed transitions, it is a simple task to derive β figures. Inter-electronic repulsion forces are reduced by varying amounts when covalent bond formation occurs.

The expansion which results may be correlated with the extent to which covalent bonds are formed in the complex. The ratio, β, is used as a measure of the tendency of a ligand to form covalent bonds. Arrangement of β values, in order of magnitude, gives rise to the Nephelauxetic series (100). As β decreases, covalent complexing power ~~also~~ increases.

The x axis of the Tanabe-Sugano energy level diagram is measured in units of $\frac{Dq}{B}$. Again by reference to absorption bands, a value can be found for this ratio. Knowing B, it is possible to calculate a value of Dq.

An example of one such calculation is given below:

Nickel (II) chlorotetrafluoroborate in ether

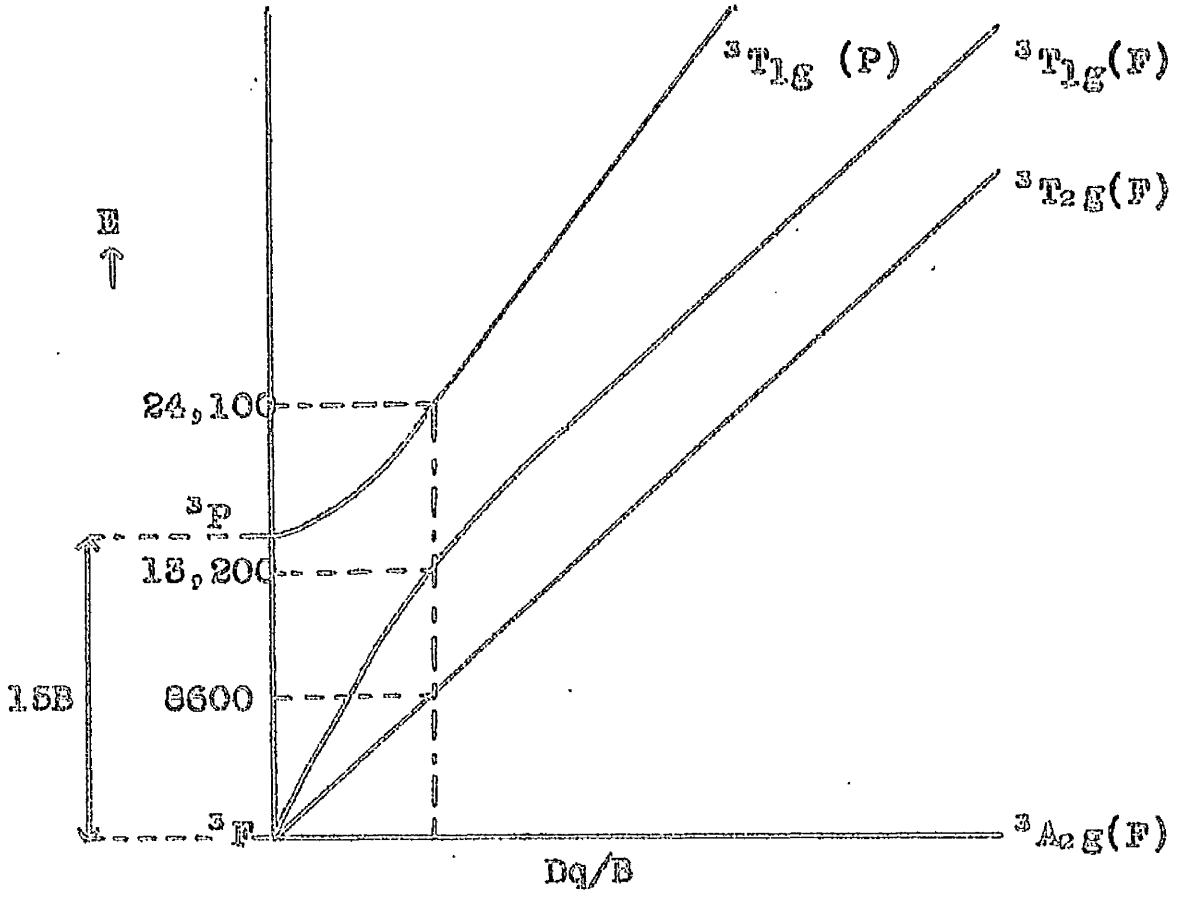
The transitions which occur are:-

$^3\emptyset A_2g(F) \rightarrow {}^3T_2g(F)$ at 8,500 cm^{-1}

$\rightarrow {}^3T_1g(F)$ at 13,200 cm^{-1}

$\rightarrow {}^3T_1g(P)$ at 24,100 cm^{-1}.

The Tanabe - Sugano diagram for the d^9 configuration (modified)



The diagram above has been simplified to show only the triplet-triplet transitions required for the calculation.

The levels associated with the ^3F and ^3P states are drawn accurately. The $^3T_{1g}(P)$ level is placed on a sliding scale and the three F levels on a fixed scale. Measurement is made along the $\frac{Dq}{B}$ axis until a fit is obtained for the (F) -> (F) transitions.

At this stage the ^3P level is adjusted to fit the third triplet-triplet transition. The separation $^3F - {}^3P$ is then found using the same units. This value (14,000cm^{-1}) is equal to 15 B and hence B can be found (933 cm^{-1}). The distance along the $\frac{Dq}{B}$ axis is then found (.925 units) and the value of Dq calculated (863.0 cm^{-1}). The value of B^1 for the gaseous Ni^{2+} ion is 1041 cm^{-1} and hence the value of β is $\frac{933}{1041} = 0.90$.

The following tables summarise the results of this and similar calculations carried out for ether and nitromethane. Since the data on benzene solutions are not so complete because of the low solubility of some of the solutes, a comparison study on this solvent could not be made.

Ligand Field Values.Cobalt (11)

Compound	Ether			Nitromethane		
	Δ (kK)	B (K)	β	Δ (kK)	B (K)	β
$Co(Cl)ClO_4$	7.20	800	0.73	9.23	900	0.82
$Co(Cl)O_2C.CF_3$	7.70	855	0.76	9.40	917	0.83
$Co(Cl)BF_4$	7.89	875	0.68	9.56	935	0.85
$Co(ClO_4)_2$	8.08	850	0.77		(a)	
$Co(O_2C.CF_3)_2$	8.39	885	0.86		(a)	
$Co(BF_4)_2$	-	-	-		(a)	

(K = cm^{-1}. kK = 1000 cm^{-1})

(a) The B and β values calculated for cobalt (11) are based on the positions of three transitions.

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ 8-9,000cm^{-1}

$\rightarrow {}^4A_{2g}(F)$ 16-18,000cm^{-1}

$\rightarrow {}^4T_{1g}(P)$ 20-21,000cm^{-1}

The last two transitions frequently occur in close proximity so that the observed band consists of a main peak and a shoulder. The exact position of the shoulder is somewhat difficult to assess and thus B and β values for cobalt are tentative in magnitude but not in order of magnitude.

The shoulder was not observed in the spectra of cobalt (11) bisperchlorate, bistrifluoroacetate or bistetrafluoroborate solutions in nitromethane.

Ligand Field Values. Nickel (11)

Compound	Ether			Nitromethane		
	Δ (kK)	B (K)	β	Δ (kK)	B (K)	β
$Ni(Cl)ClO_4$	8.16	986	0.95	8.52	940	0.90
$Ni(Cl)O_2C.CF_3$	8.35	967	0.93	8.50	1000	0.96
$Ni(Cl)BF_4$	8.63	933	0.90	8.80	933	0.90
$Ni(ClO_4)_2$	7.31	943	0.90	8.60	983	0.94
$Ni(O_2C.CF_3)_2$	7.80	947	0.91	8.70	967	0.93
$Ni(BF_4)_2$	-	-	-	8.93	955	0.92

Ligand Field Values . Chromium (111)

Compound	Ether △ (kK)	Ether B (K)	Ether β	Nitromethane △ (kK)	Nitromethane B (K)	Nitromethane β
$Cr(ClO_4)_3$	16.0	715	0.76	17.1	745	0.81
$Cr(O_2C.CF_3)_3$	16.3	730	0.80	17.1	745	0.81
$Cr(BF_4)_3$	-	-	-	16.7	745	0.81
$Cr(O_2C.CF_3)_3$ / Benzene				△ = 15.9 B = 750 β = 0.82		

For cobalt (11) and nickel (11) solutions, there is an increase in Dq values in the order $ClO_4^- \leq O_2C.CF_3^- < BF_4^-$. There is also a significant increase in the splitting energy as the solvent changes from ether to nitromethane. This may be explained on the basis of increasing dielectric constant on going from ether to nitromethane, the more polar solvent having a greater perturbing influence on the metal ion.

The corresponding values for octahedrally co-ordinated water molecules attached to the three ions studied are given in the table below.

	△	B	β
$Ni^{2+} \leftarrow 6H_2O$	8.5	940	0.89
$(6F^-)$	7.3	960	0.91
$Co^{2+} \leftarrow 6H_2O$	9.3	-	-
$Cr^{3+} \leftarrow 6H_2O$	17.4	725	0.79
$(6F^-)$	15.2	820	0.89

Units as before.

Comparison of the Δ values for the systems studied in this project, places these systems in the same region of the spectrochemical series as water but above the fluoride ion. The Δ values calculated in the present work may contain contributions from both the solvent and anions. It is not possible to determine accurately the extent to which the total splitting is affected by each perturbing entity, since it is not known, with absolute certainty, the method or magnitude of anionic co-ordination.

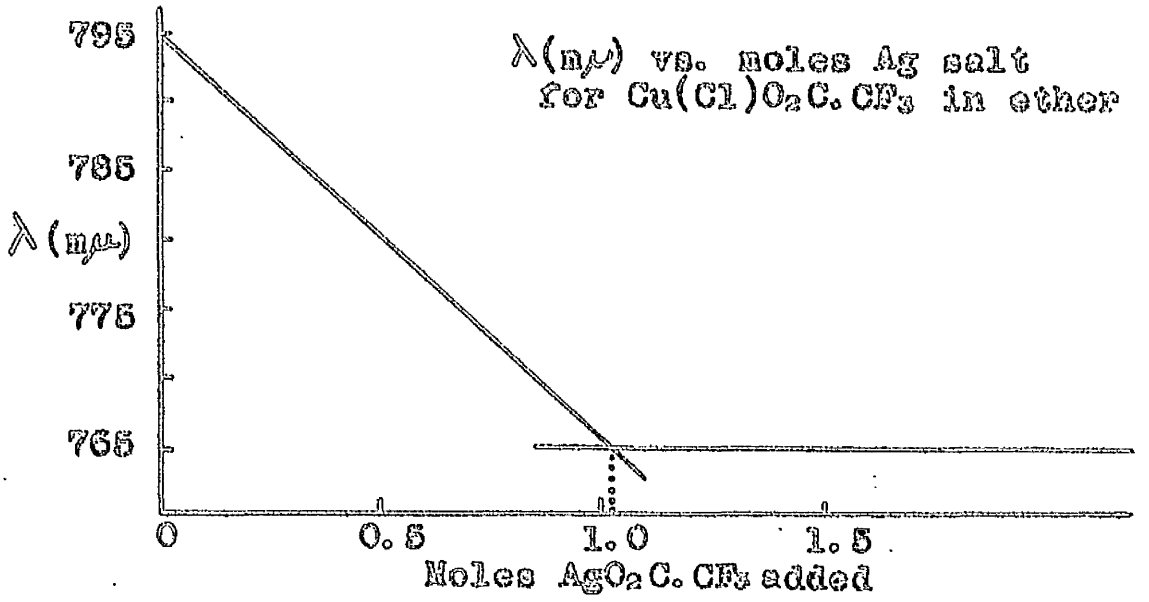
From the β values, it may be deduced that the systems studied in the present work lie above fluoride ion and water but below cyanide ion in the nephelauxetic series of ligands (79).

Spectroscopic titrations

The changes in the absorption spectra of copper (II) solutions (prepared by metathesis), accompanying the addition of the appropriate silver salt, were measured. Analysis of the solution gave the weights of copper and chlorine present. A standard solution of silver salt in the same solvent was then prepared. Aliquots of silver salt solution were added and, after filtration, the absorption spectrum measured. This last step was repeated until no further change occurred. Titration beyond this point resulted only in a reduction in optical density. The position of the maximum remained unaltered. The final positions of the bands have been reported previously in this chapter.

It was realised that this method has failings. In effect, this technique measured the appearance of a peak due to the bis-perchlorate, -trifluoroacetate or -tetrafluoroborate as well as the simultaneous disappearance of the band due to the corresponding chloro-compound. When the two bands were close together, the maximum observed contained contributions from both species.

Since the ε max. values for the bands were similar, the maximum would be expected to shift in an approximately linear manner as the titration proceeded. Where the two bands were further apart, it was found very difficult to assess the exact position of the maximum. It may be recalled that d-d transitions in Cu(11) solutions appear as broad bands. An example of a graph showing linear shift of the maximum is shown below:



Two reports (101) claim the formation of complex perchlorato compounds, e.g. $LiZn(ClO_4)_3$, $NH_4Al(ClO_4)_4$, in liquid sulphur dioxide and consequent isolation of the solid by evaporation of the solvent.

The formation of similar complexes in the perchlorate solutions described in this project should be readily recognised in the electronic absorption spectra. Since no further change in the maxima takes place on titration of the perchlorate solutions with silver perchlorate after the equivalence point is reached, it must be concluded that anionic perchlorato complex formation does not occur in these solutions.

The following table summarises the results for copper (ll) solutions. The equivalent of silver salt required for complete removal of chloride ion is calculated at the point at which no further change in the spectrum is observed.

Anion	Moles Silver Salt to Equivalence		
	Ether	Benzene	Nitromethane
$(Cl)ClO_4^-$	1.03	(b)	1.02
$(Cl)O_2C.CF_3^-$	1.01	1.04	1.06
$(Cl)BF_4^-$	1.02 (a)	-	1.05

(a) This value was calculated from the weight of silver chloride produced on addition of silver tetrafluoroborate in ether. It may be recalled that copper (ll) bistetrafluoroborate is insoluble in ether and hence titration with silver salt results in a clear solution containing no copper at equivalence.

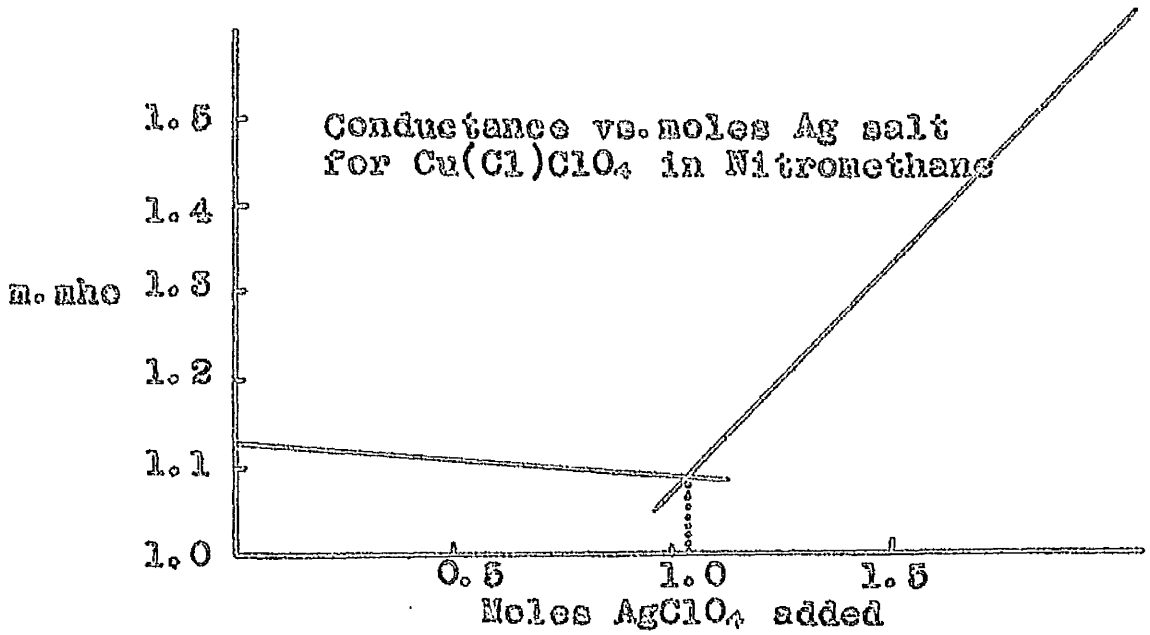
(b) It was not found possible to measure the changes in the spectrum of this solution since decomposition, to give a dark precipitate and a clear solution, was occurring throughout the titration.

Conductivity Measurements

In order to investigate the relationship between the chloroperchlorates, chlorotrifluoroacetates and chlorotetrafluoroborates and the corresponding bis-compounds, conductivity experiments were carried out in nitromethane solution. It is well-known that the conductivity of a solute in a non-aqueous solvent is subject to variation on standing (102). Since the measurements carried out were subject to some time delay between steps, it was not possible to measure accurately the molar conductivity of the solutes used during the tests. The figures quoted are therefore relative conductances.

It was believed that titration of the solution of e.g. copper (ll) chlorotrifluoroacetate in nitromethane, using a solution of silver trifluoroacetate in the same solvent, might show a change in conductance when all the chloro-species was converted to bistrifluoroacetate. Since the results from the spectroscopic titrations showed the absence of anionic perchlorato-complex formation, it is assumed that an increase in conductivity after the equivalence point would be due to the presence of silver salt.

Conversion of copper (11) in salts of the type Cu(Cl)X to CuX_2 in nitromethane resulted in conductivity plots which were very similar to each other. The solution of silver salt added was made approximately ten times the strength of the transition metal salt solution in order to minimise dilution effects. A typical graph is shown below.



Results from the copper (11) solutions in nitromethane are summarised in the table. The graphs of conductance vs. added silver salt were similar in all three cases.

Compound	Moles Silver Salt to Equivalence
$Cu(Cl)ClO_4$	1.03
$Cu(Cl)O_2C.CF_3$	1.03
$Cu(Cl)BF_4$	1.05

Attempts were made to repeat these conductivity titrations using ether as solvent. The pattern of the plots was identical to those already described although the values of conductance were much lower.

Similar experiments carried out on the nickel (11) and cobalt (11) chloro-perchlorates, -trifluoroacetates and -tetrafluoroborates in nitromethane gave results which confirmed the presence of an equilibrium mixture in solution. The results are summarised in the table:

Anion	Moles Silver Salt to Equivalence	
	Cobalt (11)	Nickel (11)
$(Cl)(ClO_4)$	0.74	0.82
$(Cl)(O_2C.CF_3)_2$	0.77	0.85
$(Cl)(BF_4)$	0.72	0.81

Conductivity measurements in nitromethane have been used to establish the number of ions present in solution. (71, 69).

Molar conductivity values of ~100, 170-200 and ~250 Mho.cm^2.$mole^{-1}$ are taken to indicate the presence of 1:1, 1:2 and 1:3 electrolytes respectively. The cell used in the present work was designed to measure relative conductivities and would require some modification before it could be used for accurate molar conductivity determinations. It would be interesting to examine solutions of transition metal salts of strong acids in nitromethane as the results could furnish important evidence as to the role of the anion in co-ordination.

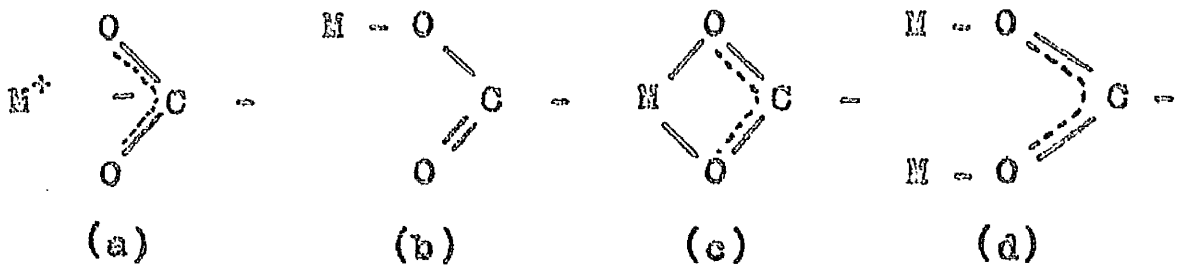
Infra-red Spectroscopy

The infra-red spectra of the solid trifluoro-acetates have been measured in the region 4000-400cm^{-1} in the hope that an investigation of the carboxylate group vibrations would yield some information as to the nature of the bonding of the metal to the trifluoro-acetate group.

The presence of α halogen atoms in an organic acid causes the carbonyl stretching vibration to move to higher frequencies, the magnitude of the shift increasing with increasing electronegativity of the halogen atom (105.)

When ionisation occurs in a carboxylic acid, the characteristic carboxylate absorption at $\sim$ 1750cm^{-1} disappears and is replaced by two bands arising from the symmetrical and asymmetrical stretches of the COO^- group. These bands normally occur in the regions 1610-1550cm^{-1} and 1400-1300cm^{-1} corresponding to the anti-symmetrical and symmetrical vibrations of the COO^- group respectively.

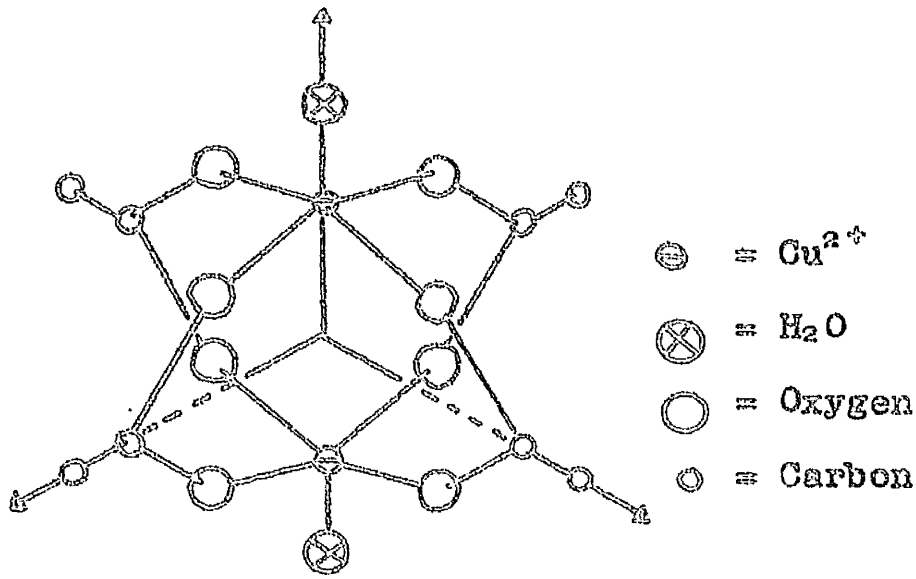
Metals can co-ordinate to a carboxyl group in several ways:



(a) (b) (c) (d)

The structure of sodium formate has been shown by x-ray analysis to be form (a). Lithium acetate dihydrate contains different C-O bond lengths indicating structure (b). Zinc acetate dihydrate has been reported to be type (c)(106). It is possible that some anhydrous acetates e.g. chromium (111) acetate have this structure. The arrangement of the oxygen atoms of the carboxyl groups round the chromium ion in an octahedral configuration satisfies the normal co-ordination number of the metal. Structure (c) has been found present (107) in the dimers, chromium (11) acetate monohydrate and copper (11) acetate monohydrate.

In the copper (11) compound, both copper atoms are in 'octahedral' environments. Each copper atom occupies one of the axial sites of the other octahedron, the other axial sites being filled by the water molecules.



Copper (11) acetate monohydrate.

The equatorial positions are filled by oxygen atoms from the carboxyl groups forming O-C-O bridges between the two copper atoms. Metal-metal bonding has been described for the above dimers and this is supported by the magnetic moments of the copper (11) complex (1.43 B.M.) and by the diamagnetism of the chromium (11) compound (115). Silver heptafluorobutyrate has also been shown to be type (d) (8) and it is possible that silver trifluoroacetate has a similar structure.

Assuming free rotation of the trifluoromethyl group, the symmetry of the acetate and trifluoroacetate ions is C_{2v}. The lack of symmetry, together with the complications arising from the number of atoms in the groups, makes distinguishing between the structures, by examination of the spectra, a difficult task. On the other hand, the spectra of a group of compounds all having the same structure might be expected to show frequency shifts, in the COO^- vibrations, as the metal is changed.

The asymmetrical and symmetrical COO^- vibrations recorded for the trifluoroacetates studied in the present work are given in the table below. Frequencies are reported in cm^{-1}.

(COO^-) Vibrations of Transition Metal Trifluoroacetates

Metal	$\nu_{as}(COO^-)$	$\nu_{s}(COO^-)$
Mn(II)	1696(s), 1655(s)	1435 (m)
Co(II)	1660(br)	1440 (m)
Ni(II)	1710(s), 1670(s)	1445 (m)
Cu(II)	1690(s), 1650(s)	1475 (m)
Zn(II)	1680 (s)	1449 (m)
Fe(III)	1666(br)	1465(m), 1430(m)
Cr(III)	1675(br)	1435 (m)
Cu^{-Cl}	1681(s), 1620(s)	1465(m), 1435(m)

(s = strong, m = medium, br = broad, sh = shoulder)

Vibrations of other Trifluoroacetates in the region 2000 - 1400cm^{-1}.

Compound	ν_{as} (COO^-)	ν_s(COO^-)	C = O str.	
Ag(1)	1677(s), 1625(s)	1460(m)		
AgH	1686(s)	1435(m)		
Na	1675(s)	1445(m)		
K	1675(s)	1445(m)		
Rb	1690(sh)1675(s)	1425(m)		
Cs	1675(br)	1420(m)		
Free acid			1825	(108)
Ethyl ester			1780	
Anhydride			1884,1818	

AgH = Silver heptafluorobutyrate.

The asymmetrical COO^- vibration in the spectra of the transition metal trifluoroacetates gives rise to very broad bands almost all of which show considerable splitting. In contrast, the corresponding bands from the alkali metal salts are much more narrow. The only indication of any splitting is found in the presence of a shoulder at 1690cm^{-1} in the rubidium salt. Nakamoto et al (109) studied the carboxyl group vibrations of a number of metal salts of carboxylic acids. From their results, they conclude that the positions of the vibrations of carboxyl group do not follow an Irving-Williams order of metals. Because of the splittings in the asymmetric vibration, it is difficult to draw any conclusions on the metal tri-

trifluoroacetates studied.

The trifluoromethyl group gives rise to a series of bands in the region 1200-1000cm^{-1}. In addition to these, three strong peaks are observed below 1000cm^{-1} in the spectra of all the trifluoroacetates studied. The positions of these peaks are tabulated below.

Infra-red spectra in the region 900-700cm^{-1}.

Metal	A	B	C
	C-C stretch	sym. CF_3 def.	$C\begin{matrix}=O\\-O\end{matrix}$ def.
Mn(11)	847	796	735, 726
Co(11)	855	795	730
Ni(11)	850	795	733
Cu(11)	860	792	730
Zn(11)	855	792	722
Cr(111)	845	795	724
Fe(111)	850	792	725
Ag(1)	850	790	727
Na	845	805	722
K	835	802	722
Rb	833	803	720
Cs	835	803	722
AgH	821	761	721
Cu—Cl	855	798	727

The assignments of these bands are tentative. From a study of trifluoroacetic acid (110, 120), partial assignment was made for bands in the region 850-600cm^{-1} and these are listed below:

625 cm^{-1} - symmetrical C-C stretch,

708 cm^{-1} - C$\overset{O}{\diagdown\!\!\diagup O}$ deformation.

The band appearing ~640 cm^{-1} in the trifluoroacetates studied is assigned to the former vibration. Bellamy and Branch (121) studied a number of compounds containing the CF_3-CF grouping and assigned a band at ~750 cm^{-1} to a CF_3 symmetrical deformation. Loos and Lord (137) studied the infra-red spectrum of perfluoroacetyl fluoride and found that this last-named vibration gave rise to a band at 760 cm^{-1}. The spectrum of silver heptafluorobutyrate shows a band at 761 cm^{-1} which must also be assigned to the CF_3 deformation. By comparison of the spectra of the trifluoroacetates shown in the table, band (B) ~790cm^{-1}, is assigned to this vibration and band (C) ~725 cm^{-1} to the C$\overset{O}{\diagdown\!\!\diagup O}$ deformation.

The above descriptions are approximate and serve only to label the three bands which appear in this region.

It is immediately obvious that there is a marked similarity between the divalent transition metal trifluoroacetates in all three vibrations. A comparable grouping can be made which includes the alkali metal trifluoroacetates. There are, however, significant differences between the two groups. These differences may be based on the position of the CF_3 group vibration (B). The following table showing separation of the three bands serves to illustrate this point. Figures are in cm^{-1}.

Metal	A - B	B - C
Mn(II)	48	61
Co(II)	50	65
Ni(II)	55	62
Cu(II)	68	62
Zn(II)	57	70
Na	40	83
K	33	80
Rb	30	81
Cs	32	80

A polynuclear structure has been suggested for copper (11) bistrifluoroacetate (111). If this is the case, it would be reasonable to suppose that the other divalent transition metal trifluoroacetates have similar structures. These, in turn, will differ from the structures of the alkali metal trifluoro-acetates which may be considered as purely ionic.

The infra-red spectra of copper (11) bistetra-fluoroborate and bishexafluoroantimonate have been measured. These solids were unfortunately mixed with silver chloride because of the method of preparation but the latter compound does not interfere with the spectra.

Copper (11) bistetrafluoroborate

In the free tetrafluoroborate ion which has T_d symmetry, two bands normally appear. The asymmetric B-F stretch, ν_3, results in a strong broad band in the region 1150-1000 cm^{-1} and the asymmetric bend, ν_4, in a weaker band $\sim$530cm^{-1}. Both these bands may be slightly split due to the presence of the two isotopes of boron, (113) or to site symmetry. A third band is often observed $\sim$ 770 cm^{-1} due to the symmetric B-F stretch, ν_1, but this is very weak, being normally infra-red inactive. When the tetrafluoroborate group is covalently bonded to a metal atom, the symmetry of the group is reduced to C_{3v} or C_{2v} depending on whether the group acts as a

mono- or bidentate ligand respectively. The effect of this change in symmetry is observed clearly on examination of the infra-red spectrum. The ν_3 band splits into a number of components, the ν_1 band becomes clearly infra-red active and the ν_4 band moves to lower frequency (14).

The ν_4 band observed in copper (II) bistetrafluoroborate is split into two components at 1080, 1050 cm^{-1}. A medium band appears at 730cm^{-1} which can be assigned to the ν_1 mode and a strong, broad band is observed at $\sim$510 cm^{-1}. This last band is unresolved. While the splitting of the ν_4 band is not so evident as in trimethyltin tetrafluoroborate (14,89), it may be concluded that some covalent bonding occurs between the tetrafluoroborate group and the copper.

The ν_3 vibration for the SbF_6^- ion is observed (122) at 660 cm^{-1}. In trimethyltin hexafluoroantimonate (14) this band is resolved into three components at 675, 656 and 640 cm^{-1}. In the spectrum of the copper compound, splitting occurs to give two bands at 656 and 624 cm^{-1}. It was difficult to find any trace of the band between 480 - 440 cm^{-1} assigned (14) to the ν_4 mode. Some interaction between the metal and the hexafluoroantimonate group is however indicated by the splitting of the ν_3 band.

Magnetic Studies

Magnetic Studies

Magnetic measurements have been used in inorganic chemistry mainly to investigate valency and stereochemical problems in transition metal complexes. The presence of unpaired electrons in the metal ion leads to paramagnetism which can be detected and measured by a variety of methods. The information which can be obtained from investigation of the magnetic properties of transition metal compounds, is, of course, dependent on the accuracy with which the measurements can be made. This, however, must be coupled with the interests of the investigator who may be concerned only with a large alteration in magnetic moment on changing from one stereochemistry to another.

Several recent and excellent reviews cover the subject of magnetochemistry (116,117).

In the present work, magnetic measurements have been made both on the solid trifluoroacetates which have been isolated, and on some of the solutions described in Chapter I. This investigation, together with the data from the electronic absorption spectra, would give, it was hoped, a confirmation of the stereochemistry proposed for the compounds studied.

(a) Solutions

(a) Solutions

Measurement of magnetic susceptibilities of the solutions of paramagnetic ions was made by the method of Evans (118). The position of a line in the proton resonance spectrum depends on the bulk susceptibility of the medium in which it is situated. For an inert substance in solution, the shifts caused by paramagnetic ions are given by:

$$\frac{\Delta H}{H} = \frac{2\pi}{3K}$$

A dilute solution of a paramagnetic substance containing about 2% of an inert reference (e.g. tetramethyl silane) is put into a nuclear magnetic resonance tube together with a capillary containing the solvent and the same concentration of reference. On spinning the tube, two proton resonance lines will be obtained from the tetramethyl silane. These lines are obtained because of the difference in volume susceptibility between the solution and the solvent with the line from the former lying at higher frequency. The mass susceptibility, χ, is then given by:-

$$\chi = \frac{3}{2\pi} \cdot \frac{\Delta f}{fm} + \chi_o + \chi_o \cdot \frac{do-ds}{m}$$

where: Δf is the separation between the two lines in cycles. $sec.^{-1}$,

f is the frequency at which the proton resonances are being studied, in cycles, sec^{-1},

m is the mass of substance in 1 ml. of solution,

χ_o is the mass susceptibility of the solvent,

do is the density of the solvent,

ds is the density of the solution.

From the value of χ, the magnitude of the molecular susceptibility can be calculated by simply multiplying by the molecular weight. After correction for diamagnetic susceptibility, the resulting value is symbolised χ^1_m. This in turn is related to the magnetic moment, μ_{eff}, by the formula:-

$$\mu_{eff.} = 2.84\sqrt{\chi^1_m \times T} \quad \text{Bohr Magnetons,}$$

where T is the temperature in °K.

The spinning side-bands which frequently appear tend to make the spectra overcomplicated. These side bands can be recognised by altering the spinning rate. This changes the frequency at which these bands appear but leaves unaltered the signals from the solution and solvent.

Magnetic Moments of Solutions

(1) Copper (II) Solutions.

Anion	Ether	Benzene	Nitromethane
$(Cl)(ClO_4)$	2.06 B.M.	-	1.84 B.M.
$(ClO_4)_2$	1.91 B.M.	-	1.92 B.M.
$(Cl)(O_2C.CF_3)$	1.78 B.M.	$\leqslant$ 0.5 B.M.	1.85 B.M.
$(O_2C.CF_3)_2$	1.62 B.M.	$\leqslant$ 0.5 B.M.	1.78 B.M.
$(Cl)(BF_4)$	$\leqslant$ 0.5 B.M.	-	$\leqslant$ 0.5 B.M.
$(BF_4)_2$	-	-	$\leqslant$ 0.5 B.M.

The ether and nitromethane solutions show magnetic moments within the range experimentally found for Cu^{2+}. The benzene solutions of the chloro-trifluoroacetate and bistrifluoroacetate gave virtually no shift of the solvent peak. The solutions of these compounds in benzene were of similar strengths to the corresponding ether and nitromethane solutions. Thus the absence of a shift was not due to dilution. Even when the scale factor was reduced to 0.25 c.p.s. per unit (the maximum expansion possible), it was extremely difficult to measure any separation of the peaks. It must be concluded that very weakly paramagnetic ($\leqslant$0.5 B.M.) or diamagnetic species are present in solution.

This is somewhat surprising since the solid compound, copper (II) bistrifluoroacetate, has a magnetic moment of 1.81 B.M. corresponding to one unpaired electron.

Low results obtained from the tetrafluoroborate solutions in ether and nitromethane also may be due to diamagnetic or weakly paramagnetic species although the magnetic moment of solid copper (II) bistetrafluoroborate is not known.

Recently the temperature-dependence of the magnetic moment of copper (II) bistrifluoroacetate has been investigated (111). The authors suggest that, unlike copper (II) acetate monohydrate, which has been shown (107) to be dimeric, the bistrifluoroacetate is more polymeric. The increased separation of the copper (II) ions resulting from this polymerisation is regarded as explanation of the 'normal' magnetic moment of 1.81 B.M. compared with 1.43 B.M. found in the acetate monohydrate. A remarkable change must take place on dissolving the chloro- and bis-trifluoroacetates of copper (II) in benzene.

In a recent review (119) on copper (II) compounds with subnormal magnetic moments, it has been suggested that there are two possible mechanisms by which magnetic moments can be decreased.

(i) Four-atom bridges

(ii) Monoatomic bridges.

Type (i) is found mainly in copper (II) carboxylates, e.g. the acetate monohydrate which is a dimer $Cu_2(O_2C.CH_3)_4.2H_2O$. The feature of this type of compound is carboxylate bridging between the two copper atoms. This effect brings the copper atoms in close proximity (2.64Å) and the interaction of the two metal atoms bring the magnetic moment down to a value of 1.43 B.M. (A similar mechanism renders the corresponding Cr(II) compound virtually diamagnetic. This low value is very surprising but the investigators offer no explanation (115).).

Compounds of type (ii) include the pyridine N-oxide complex, $CuCl_2.C_5H_5NO$ (0.73 B.M.), copper (II) oxide, (0.78 B.M.), and potassium copper (II) fluoride, $KCuF_3$, (1.38 B.M.). In these compounds, direct metal-metal interaction is absent or is less important as a mechanism for reducing the magnetic moment. The interaction, in this case, occurs between metal atoms separated by one atom which may be a monoatomic anion or the atom of an attached ligand. Reduction in magnetic moment is due to an exchange mechanism working along the chain of atoms.

The perovskite structure of $KCuF_3$, containing M-F-M-F chains, seems specially suited to this type of mechanism (119).

The formation of dimeric or polymeric structures in solution is more favoured in organic solvents than in water. In aqueous solution, breakdown to the monomeric hexahydrate ion is certain to occur. Two factors appear important in the ability of an organic solvent to affect the formation of dimeric molecules and also magnetic interaction. These are:-

(i) dielectric constant

(ii) co-ordinating power.

The power of a solvent to increase dimerisation tendencies and magnetic interaction appears to increase with decreasing dielectric constant giving rise to the series:-

water, (78.5) < pyridine (12.3) < methanol (32.6) < ethanol, (24.3) < acetone, (20.7)

< chloroform (4.8) < benzene (2.3) < dioxane, (2.2) < carbon tetrachloride (2.2) < diethyl ether (4.4) (119)

There are obvious anomalies to be observed in this series. It is surprising to find e.g. dioxane listed close to ether if co-ordinating power can be considered to have a major effect.

The magnetic moment of copper (II) bistrifluoroacetate is little different in ether solution from that in the solid state. On the other hand, copper (II) formate has a magnetic moment of 1.64 B.M. in the solid state which alters markedly (1.06 B.M.) when dissolved in dioxane. Since the dielectric constants of these two solvents are similar it is to be expected that they will have similar effects on the magnetic moment of a solid if the dielectric constant only is considered.

The co-ordinating power of the solvent must play an important part in determining the extent to which the magnetic moment is affected. Dioxane is much more strongly co-ordinating than ether and this may be the dominant factor in reducing the magnetic moment in the cases quoted. Benzene is listed in the series as being comparable with dioxane in effective power. This is acceptable on the basis of their dielectric constants (dioxane $\sim$ 2.2, benzene $\sim$ 2.3). The method of co-ordination of these two solvents is, however, markedly different and it would appear that the π bonding mechanism of benzene is comparable with the σ-bonding system of dioxane in the ability to induce a reduction in magnetic moment.

The picture is therefore somewhat complicated at the moment and is further hindered by the lack of structural evidence available on solid compounds with low magnetic moments.

It is possible that strong metal-metal interaction occurs in benzene solutions of the copper (11) carboxylates studied in this project. In the ether and nitromethane solutions of the tetrafluoroborates, the exchange mechanism may be working. Until more work is carried out on the whole subject of low magnetic moments, it will be difficult to assess exactly the true cause of the abnormality.

Magnetic Moments of other Bis-Trifluoroacetate Solutions

Metal	Ether	Nitromethane
Co(11)	3.96 B.M.	4.15 B.M.
Cr(111)	3.71 B.M.	3.92 B.M.
Ni(11)	3.24 B.M.	3.07 B.M.
Mn(11)	5.5 B.M.	5.5 B.M.

As with the corresponding copper (11) examples, these solutions contain metal atoms which have magnetic moments corresponding to high-spin octahedral configurations. This confirms the interpretation of the electronic absorption spectra of the solutions.

(b) Solid Trifluoroacetates - Gouy method

The magnetic moments of the solid trifluoroacetates were measured using this method. Samples were packed into a tube fitted with a ground glass stopper in order to exclude moisture. The standard used was mercuric cobaltithiocyanate, $Hg[Co(CNS)_4]$.

Magnetic Moments of Solid Trifluoroacetates

Compound	μ eff (B.M.)	Spin-only value (B.M.)	Range Found (B.M.)
$Cr(O_2C.CF_3)_3$	3.85	3.88	3.7 - 3.9
$Fe(O_2C.CF_3)_3$	5.72	5.92	5.7 - 6.0
$Mn(O_2C.CF_3)_2$	5.50	5.92	5.65 - 6.10
$Co(O_2C.CF_3)_2$	4.65	3.88	4.3 - 5.2
$Ni(O_2C.CF_3)_2$	3.11	2.83	2.8 - 3.5
$Cu(O_2C.CF_3)_2$	1.80	1.73	1.7 - 2.2
$Cu(Cl)(O_2C.CF_3)$	1.75	1.73	-

The magnetic moments are in good agreement with the concept that the complexes are high-spin (weak field) octahedral compounds.

Summary

The electronic absorption spectra of the ether, benzene and nitromethane solutions of transition metal perchlorates, trifluoroacetates and tetrafluoroborates are consistent with the concept that the metal atoms in solution are in octahedral environments. Because of John-Teller distortion, variations from strictly octahedral symmetry are to be expected. This is especially marked in copper (11) and less noticeable in e.g. titanium (111) and iron (11).

The effect of different solvents on the absorption spectra of a given metal ion has been studied by many workers. The values of Δ, which can be calculated from the position of d-d bands, place the ligands relatively in the spectrochemical series. The factors which contribute to the magnitude of Δ have already been mentioned. Since the purely electrostatic perturbation contributes least to the total splitting, it would seem that an explanation of the increase in values of Δ on moving from ether to nitromethane based on an increase in dielectric constant ($\sim$4 for ether, $\sim$36 for nitromethane) would be a simplification although both possess o lone pairs.

The position of benzene in this 'spectrochemical series' is rather uncertain. In some instances, it may be ranked with ether and this would be in accord with its dielectric constant (~ 2). In other cases, the Δ values are remarkably different, e.g. in Ti(III). It is not reasonable, however, to compare two systems having markedly different bonding properties. It is well-known that π-bonding has a drastic effect on Δ values. The balance of the two opposing contributions from metal-ligand and ligand-metal π-bonding will be a critical factor in the final value of Δ.

The spectra also show anion dependence and it would seem that some measure of covalent bonding between the anion and the metal ion occurs in solution.

The volatility of anhydrous cupric nitrate was first shown by Addison and Hathaway (22). It was shown later that mercuric and ferric nitrates behaved similarly (113) although nitrates of nickel, zinc, cobalt, etc. did not. Since cupric and ferric perchlorates are volatile (103), it would be reasonable to suppose that they can exist, in the vapour phase, as molecules. If this is true, then some degree of covalent bonding must exist between the perchlorate group and the metal ion. This is not normal for the perchlorate ion since most perchlorates have been considered purely ionic.

The perchlorate ion is tetrahedral and, if covalent bonding is present, co-ordination could be expected to occur through one (monodentate)or two (bidentate) oxygen atoms of each perchlorate group. From a study of the infra-red spectra of hydrated and anhydrous perchlorates (103), Hathaway and Underhill concluded that the perchlorate group acted as a bidentate ligand. The same authors reported the results of a study of $Cu(ClO_4)_2$ and $Cu(BF_4)_2$ in methyl cyanide and ethyl acetate solutions(104). They suggest that in methyl cyanide solutions, the copper ions are solvated by six solvent molecules. In ethyl acetate, it is proposed that solvation, by four molecules of solvent, occurs on the equatorial plane and that the axial positions are occupied by weakly co-ordinated anions.

It seems reasonable to suppose that, in solutions of anhydrous transition metal perchlorates and tetrafluoroborates in weakly basic organic solvents, bonding occurs from the anions as well as from the solvent molecules. From the infra-red spectra of the trifluoroacetates, it would appear that the bonding in the transition metal compounds differs from that in the alkali metal salts. Since the latter salts are almost certainly ionic, it may be suggested that some degree of covalent character exists in the metal-carboxyl bonds.

The reflectance spectra of the solid trifluoroacetates indicate that the metal atoms in these compounds are octahedrally co-ordinated. In the bis-compounds this may be achieved by carboxylate bridging. The chloro-compounds may contain chlorine and carboxylate bridges.

The existence in solution of species of the formula M(Cl)X, where X is the strong acid anion, has been established. Further evidence on this type of compound has been found by Henry (114) who has prepared complexes of the type $Cu(Cl)BF_4.(SbPh_3)_4$, $Cu(Cl)BF_4.(AsPh_3)_4$ and $Cu(Cl)ClO_4.(C_8H_{14}O_3P)_4$ where $C_8H_{14}O_3P$ is 4-methyl - 2,6,7, trioxa - 1, - phosphabicyclo [2,2,2, octane], by adding weak ligands to copper (II) solutions obtained by metathesis.

It is obvious that solutions such as are described in Chapter I have a useful place in some branches of synthetic chemistry especially where weakly basic ligands are being used and also where anhydrous conditions are mandatory if complex formation is to take place.

Experimental.

1. Absorption Spectra

The ultra-violet and visible spectra of the solutions were measured on an Optica CF4. spectrophotometer using 1 cm. ground-glass stoppered cells. For the Ti(III) and Fe(II) solutions, cells were designed so that the spectra could be measured under nitrogen. Filtration of the above mentioned solutions was carried out under dry nitrogen. Diagrams of the apparatus are given at the end of this section (Appendix I). Optical densities in the region 50,000 - 10,000 cm^{-1} were checked using a Hilger Uvispek H 700.307 Spectrophotometer. This procedure was necessary when the 100% control of the Optica intrument was altered so that charge transfer bands were reduced in intensity and could be measured accurately along with the d-d transitions. Reflectance spectra were also measured on the Hilger instrument.

2. Infra-red spectra

Spectra in the region 4,000-400cm^{-1} were measured using a Perkin-Elmer 125 Grating Spectrophotometer. Mulls were prepared using Nujol or hexachlorobutadiene and sample preparation and mulling carried out in the dry-box.

5. Magnetic measurements

(a) Solutions

Measurements were made on a Perkin Elmer R.10 spectrometer at 40.004 Mc sec.$^{-1}$. The spinning sample tubes had an external diameter of 5.0 m.m. (i.d. 3.5 mm.) and the capillaries so constructed that the volume of liquid in the capillary was approximately equal to the volume of solution in the annulus. The capillary was filled with ether containing 2% tetramethylsilane or pure dry benzene or nitromethane. Ether solutions for magnetic measurements were prepared by metathesis using solvent containing the internal reference so that the proton lines from the solvent and solution were of equal intensity. The samples were protected from moisture by means of a plastic cap.

(b) Solids

Preparation of the solid samples is included in Chapter III. Magnetic measurements were carried out by the Gouy method. An Oertling balance capable of weighing to 0.01 mg. was used. The sample was packed into a pyrex capillary (3.5 mm. internal diameter) fitted with a ground glass stopper. All packing operations were carried out in the dry-box. The specimen was suspended by an aluminium collar hanging on a nylon thread. The strength of the magnetic field was found by calibration with $Hg[Co(CNS)_4]$.

4. Conductivity measurements

Changes in conductivity of the solutions were measured using a Wayne-Kerr Universal Bridge B.221. A cell was designed to allow measurements to be made in non-aqueous solvents. A diagram of the cell is shown in Appendix II.

All titrations were carried out in the dry-box. The cell was filled with solution until the electrodes were covered. Aliquots of silver salt solution were added through the serum cap by means of a 5 ml. Eva μ- Micromatic syringe. The cell was then removed from the dry-box and the mixture stirred for one minute using a magnetic stirrer. The electrodes were connected to the bridge and the conductivity measured.

5. Analyses

Analyses of solids and solutions were carried out by normal analytical methods. Analysis of the solutions was effected by pouring a measured aliquot on to 50 ml. water and boiling gently to remove the organic solvent, followed by determination of the metal present.

Copper (II) bistetrafluoroborate and bis-hexafluoroantimonate were obtained and analysed in the following manner.

The ether solution containing the chloro-compound was treated, in the dry-box, with the appropriate silver salt dissolved in ether until all the chloride ion was converted. The mixed precipitate of silver chloride and copper compound was filtered off using a weighed sintered crucible and washed several times with dry ether. The crucible was then placed in a vacuum desiccator and the remaining solvent removed by pumping. The crucible was reweighed and the copper compound washed into a Buchner flask using several washes of distilled water. The crucible, now containing only silver chloride, was dried and reweighed. The copper in the filtrate was estimated and the percentage copper calculated for the compound.

The corresponding cobalt (11) and nickel (11) bistetrafluoroborates were obtained in a similar manner.

Copper (11) bistetrafluoroborate

Calculated for $Cu(BF_4)_2$ Cu : 26.6%

Found Cu : 25.7%.

Copper (11) bishexafluoroantimonate

Calculated for $Cu(SbF_6)_2$ Cu : 11.9%

Found Cu : 10.3%.

Cobalt (11) bistetrafluoroborate

Calculated for $Co(BF_4)_2$ Co : 25.3%

Found Co : 24.4%.

Nickel (11) Bistetrafluoroborate

Calculated for $Ni(BF_4)_2$ Ni : 25.3%

Found Ni : 24.1%.

Silver Heptafluorobutyrate

This was prepared by adding a slight excess of silver carbonate to hexafluorobutyric acid in a platinum crucible. After filtration, the solution was evaporated to low bulk and allowed to crystallise. The solid obtained was recrystallised from water and dried by continuous pumping over phosphorus pentoxide for 24 hours. The solid was then placed over phosphorus pentoxide under vacuum for several days.

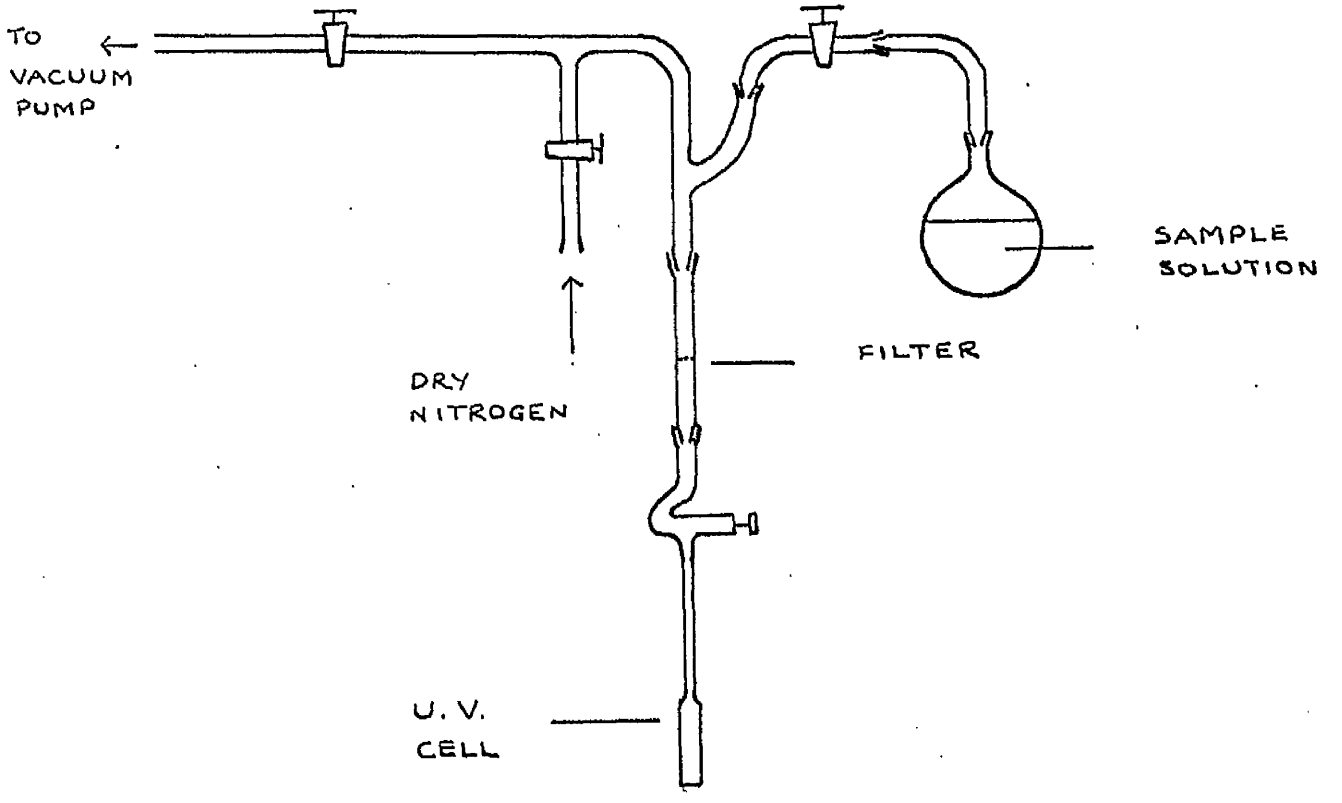
Calculated for $AgO_2C.C_3F_7$ Ag : 33.6%

Found Ag : 33.0%.

Anhydrous trifluoroacetates of sodium, potassium, rubidium and calcium.

All four anhydrous salts were prepared by the same method. A slight excess of trifluoroacetic acid was added to the metal carbonate in a platinum crucible. The anhydrous salts were then obtained as described for silver heptafluorobutyrate. Absence of hydroxyl peaks in the infra-red spectra was taken to mean that anhydrous compounds had been obtained.

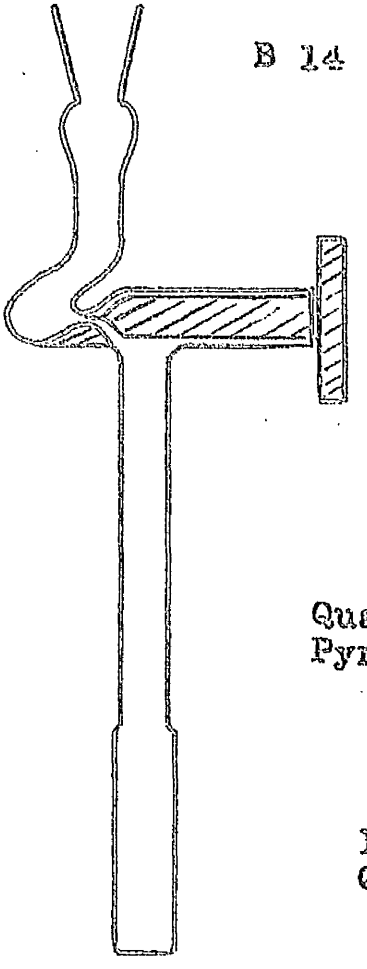
APPENDIX I

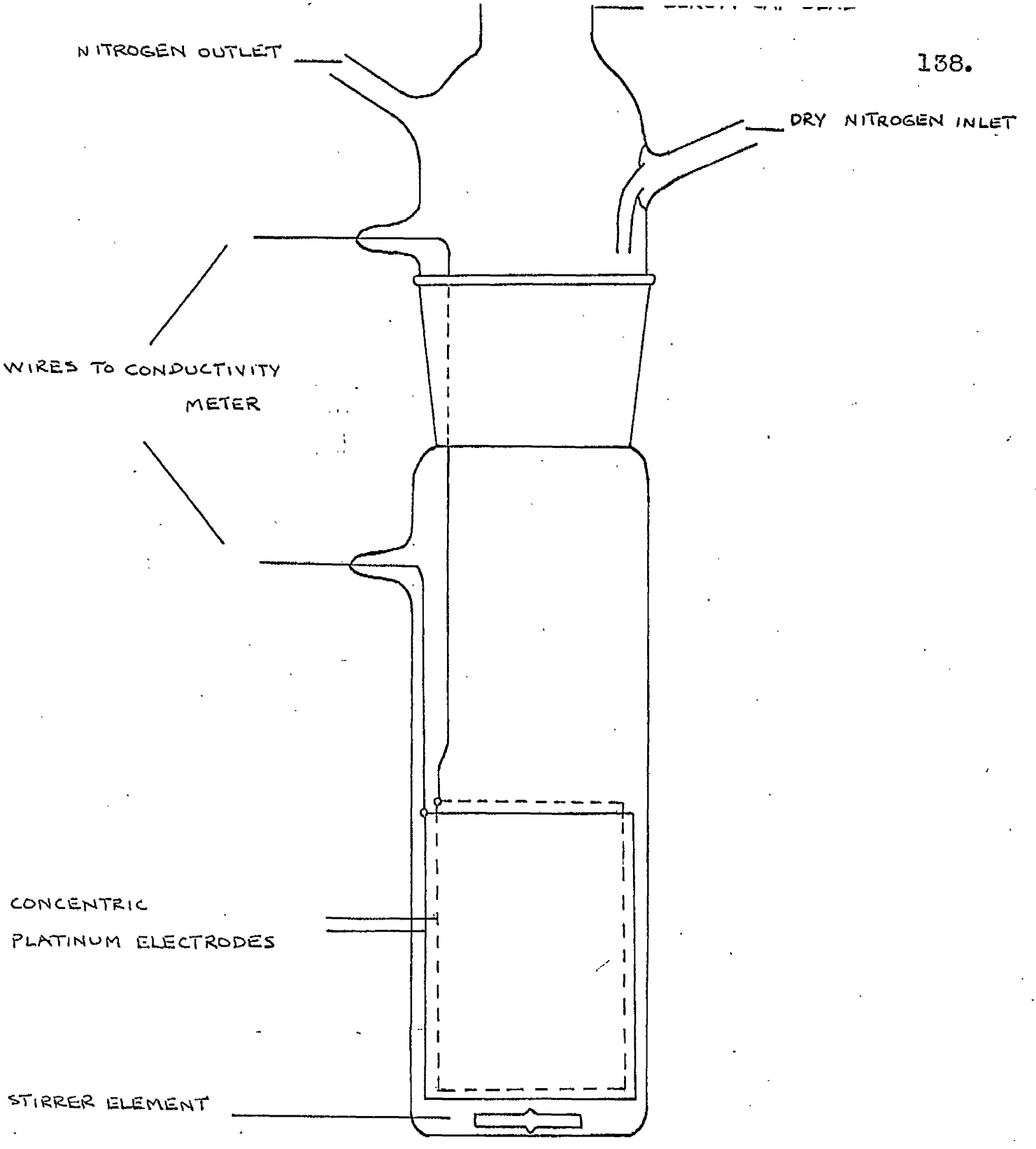


FILTRATION UNDER NITROGEN

APPENDIX IA

U. V. Cell





CONDUCTIVITY CELL.

APPENDIX II

CHAPTER III

The Preparation of Anhydrous Perchlorates, Trifluoroacetates and Tetrafluoroborates of First-Row Transition Elements.

In order to investigate the possibility of alternative methods for the preparation of the solutions described in Chapter I, attempts were made to prepare the anhydrous metal salts of the strong acids studied. The anhydrous compounds, if available, would allow a much more simple route to solution preparation and the solutions so obtained could be compared with those obtained by metathesis with regard to spectroscopic and magnetic properties, and solubility.

In general the anhydrous salts are little known whereas the hydrated forms are well established.

1. Perchlorates

The perchlorates of most metals are known, the majority in the form of the hydrate. The preparation of such hydrates is a simple procedure but until recently few salts were known in the anhydrous state. One notable exception is silver perchlorate. This salt is prepared by heating silver nitrate or silver oxide with a large excess of 72% perchloric acid (123).

The salt forms a monohydrate which can be dehydrated at 43°C. Anhydrous silver perchlorate is extremely hygroscopic. Lead perchlorate trihydrate was converted to the anhydrous compound by drying over phosphorus pentoxide over a prolonged period (67).

The hydrated perchlorates of cobalt (11), copper (11), nickel (11), manganese (11), chromium (111) and iron (111) have been prepared by reacting the metal oxide, hydroxide or carbonate with perchloric acid. After recrystallisation, the solid compounds were dried over phosphorus pentoxide. The hydrates were then set over phosphorus pentoxide in a vacuum desiccator and the vacuum maintained over several days. It was found that it was not possible to remove all the water of crystallisation by this method. Hydroxyl peaks still appeared in the infra-red spectrum of the solid samples even after two weeks standing under vacuum.

Addison and Hathaway (124) have prepared anhydrous copper (11) perchlorate by the repeated reaction of nitrosyl perchlorate on copper (11) perchlorate dihydrate. Purification by sublimation at 200°C under vacuum was effected between each stage of the reaction. Zinc perchlorate has been prepared in a

similar manner (135). Zinc oxide was treated with nitrosyl perchlorate in vacuo at 180 - 190°C. It is claimed in the report that 99% pure anhydrous zinc perchlorate was obtained. Moss (38) prepared copper (11) and iron (111) perchlorates by reacting silver perchlorate with the appropriate metal chloride in liquid sulphur dioxide as solvent. These compounds were similar in properties (volatility, infra-red spectrum) to the corresponding perchlorates prepared by Hathaway and Underhill(126). One major difference arose in that the latter authors imply that copper (11) perchlorate did not dissolve in benzene. Removal of finely divided silver halide remains a problem in metathetical preparations as described by Moss (38). The perchlorates mentioned, however, sublime fairly readily, thus providing a means of separation.

Removal of the organic solvent from a solution of an anhydrous perchlorate is an extremely hazardous operation although solutions of transition metal perchlorates in organic solvents such as nitromethane are readily available. Perchlorates are infamous for exploding when in contact with organic material. Explosion occurred during the preparation of a saturated methanolic solution of lead perchlorate (67).

2. Trifluoroacetates

Swarts (25) prepared anhydrous copper (11), silver (1), mercury (1), mercury (11), thallium (1), barium (11), aluminium (111) and nickel (11) trifluoroacetates, and the hydrated iron (11) and iron (111) salts. Of the anhydrous trifluoroacetates mentioned above, it is claimed that the copper (11), mercury (1), aluminium (111) and nickel (11) compounds are volatile. Moss (38) prepared anhydrous copper (11) bistrifluoroacetate by metathesis between copper (11) chloride and silver perchlorate in liquid sulphur dioxide. The salt could not be sublimed even at 180°C/10^{-3} mm., although Swarts reports sublimation at 180°C/1mm. without decomposition.

The trifluoroacetates of the metals described under perchlorates were prepared by methods similar to those used by Swarts (25). Copper (11), chromium (111) and nickel (11) trifluoroacetates were obtained as the anhydrous salts. The remainder crystallised, with some difficulty, as the hydrates. Total removal of the water of crystallisation could not be effected by pumping over phosphorus pentoxide except for the cobalt (11) and manganese (11) salts.

3. Tetrafluoroborates

No anhydrous first-row transition metal tetrafluoroborate is known. The silver salt has been prepared (5) and has been mentioned previously. Moss (38) failed to prepare any anhydrous salts by metathesis in liquid sulphur dioxide. The hexahydrates of most of the divalent metals of the first-row transition series are known and their structures defined(127). These are readily obtained from aqueous solution and the tetrafluoroborates of copper (11), cobalt (11), nickel (11), manganese (11) have been prepared. Chromium (111) tetrafluoroborate has also been obtained in the hydrated form. Again, phosphorus pentoxide would not remove all the water of crystallisation from these hydrates.

The ready availability of the hydrates provoked an investigation into possible methods of dehydration. Since it was not found possible to completely dehydrate by vacuum pumping over phosphorus pentoxide, attention was directed towards (i) thermal decomposition and (ii) the use of 2,2 dimethoxypropane, a dehydrating agent which has become quite popular during the last few years.

(i) Thermal Decomposition

In view of the fact that silver perchlorate monohydrate can be dehydrated at 43°C, it might be supposed that the thermal decomposition of other hydrated transition metal perchlorates would lead to anhydrous salts. Calcium perchlorate tetrahydrate, however, forms calcium chloride on heating thus showing a resemblance to the alkali metal perchlorates(128). Iron (III) perchlorate decahydrate has been stated to decompose to ferric oxide, Fe_2O_3(129). Other reports on the dehydration of perchlorates by thermal decomposition serve only to indicate that the complete removal of water is a most difficult operation if destruction of the anhydrous salt is to be avoided.

A thermogravimetric balance was used in order to investigate the decomposition of the hydrated perchlorates. Without exception, the removal of water was accompanied by either partial or total decomposition of the perchlorate ion. Even when the temperature was held constant at the initial dehydration point, continuous weight loss resulted.

Chromium (III), copper (II) and nickel (II) trifluoroacetates in the anhydrous state have been reported previously in this chapter.

Vacuum dehydration over phosphorus pentoxide of the iron(III) cobalt (II) and manganese (II) hydrates resulted in the complete dehydration of the last two compounds.

The thermal decomposition of all the trifluoroacetate hydrates gave similar results to those obtained for the perchlorates, decomposition of the 'anhydrous' form accompanying dehydration, although partial dehydration without decomposition could be effected in some cases.

The thermal decomposition of a number of hydrated tetrafluoroborates has been reviewed by Sharp (150). Divalent compounds of calcium, zinc, magnesium, barium, strontium and cobalt give the anhydrous tetrafluoroborates. The alkali metal hydrates can be dehydrated under vacuum at room temperature and the cobalt and zinc compounds by heating at 70-80° and 60° respectively.

Careful repetition of the thermal dehydration of cobalt tetrafluoroborate gave a product which certainly contained the metal tetrafluoroborate in the anhydrous form but which was contaminated with a decomposition product. This latter substance was almost certainly the fluoride since a red residue was obtained on shaking the mixture with nitromethane.

The mixture gave a broad absorption in the region 1100-1000cm^{-1} indicating the presence of the tetrafluoroborate group. Results for the other hydrated tetrafluoroborates were similar although, in the experiments with the copper (11) and nickel (11) salts, only a very small proportion of the mixture, obtained after thermal treatment, was found to be the anhydrous tetrafluoroborate.

(ii) Dehydration by 2,2 Dimethoxypropane

Erley (131) reported the use of this dehydrating agent, in drying samples for infra-red analysis in 1957. At 30°C, water reacts with 2,2 dimethoxypropane to give acetone and methanol according to the equation:-

$$(CH_3O)_2\ C.(CH_3)_2 + H_2O \rightarrow 2CH_3OH + (CH_3)_2\ CO$$

The dehydrating properties of this reagent were investigated by Starke(132) who dehydrated iron (111) chloride as a preliminary step in the preparation of iron (111) nitriloethoxide, $Fe(OC_2H_4)_3N$.

Aluminium perchlorate nonahydrate has been dehydrated using 2,2, dimethoxypropane by Franz(133). The anhydrous salt was not isolated, complex formation with pyridine being used to separate the complex $Al(ClO_4)_3.4C_5H_5N$.

The same author reports similar dehydrations with magnesium perchlorate hexahydrate and lithium perchlorate dihydrate, again without separation of the anhydrous compound.

The preparation of dimethyl sulphoxide (C_2H_6SO), tetramethylene sulphoxide (C_4H_8SO), and pyridine N-oxide (C_5H_5NO) complexes of cobalt (11), chromium (111) and nickel (11) perchlorates of the general formula $M_x(ClO_4)_x$, where x = 2 for cobalt (11) and nickel (11) and x = 3 for chromium (111), in which the first stage is dehydration by this reagent, has been reported by Meek et al(134). Several other reports on the use of 2,2 dimethoxypropane as a dehydrating agent (71, 135). combine with those already mentioned to illuminate one extremely important point. At no stage during the preparation of the complexes is the anhydrous material isolated. The reaction by-products (acetone and methyl alcohol) are well-known as solvating species and an obvious difficulty, in obtaining the pure anhydrous compound, is the removal of the attached solvent molecules. Added to this is the danger of removing organic solvent from perchlorates.

An interesting article was published recently (136) in which the preparation of anhydrous nickel perchlorate complexes with methanol and ethanol was reported. The method involves dehydration with 2,2 dimethoxypropane or 2,2 diethoxypropane as the initial stage. Precipitation of the alcohol-metal perchlorate complex is effected by adding the solution obtained after dehydration, to a large excess of dry ether. No mention is given to the properties of the solid complexes but it must be assumed that they are fairly hygroscopic since the physical measurements (infra-red, ultra-violet spectra) were carried out under anhydrous conditions.

In the present work, the hydrated perchlorates, trifluoroacetates and tetrafluoroborates of copper (11), cobalt (11), manganese (11), nickel (11) chromium (111) and iron (111) were treated with 2,2 dimethoxypropane. The solvent was removed from the trifluoroacetate and tetrafluoroborate samples by vacuum distillation. In all cases, the solid sample obtained showed an infra-red absorption, ν(O-H), at 3360-3380 cm^{-1} indicating the presence of solvated methyl alcohol. (Solvated water absorbs at 3470cm^{-1} in $[Ni(H_2O)_6][ClO_4]_2$).

Attempts to remove this by heating under vacuum always resulted in some decomposition of the parent compound.

In the case of the perchlorates, it was felt that the production of concentrated solutions was to be avoided, if possible. An attempt was made to prepare solutions in nitromethane and benzene by adding the appropriate solvent to the mixture obtained after dehydration and then removing some of the mixture by vacuum distillation. Repetition of this procedure, it was anticipated, would give a solution in pure nitromethane or benzene. The composition of the distillate was analysed by vapour-phase chromatography.

Preparation of Solutions from Dehydration Products

As previously stated, the object of the work described in this chapter was to investigate a more simple route for obtaining the solutions described in Chapter I. As a general statement, the preparation of solutions of transition metal perchlorates and tetrafluoroborates was found more difficult than by metathesis. Only in the case of the trifluoroacetates was the task simplified. Solutions of copper (11), cobalt (11), nickel (11), manganese (11) and chromium (111) trifluoroacetates were readily available since the anhydrous material was easily obtainable from the hydrate.

For manganese (11) trifluoroacetate, this method was undoubtedly superior. It may be recalled that the preparation of solutions of manganese (11) salts took some two months to reach completion.

The solutions obtained from the trifluoroacetates described above were spectroscopically identical with the bis-trifluoroacetate solutions reported in Chapter I.

(a) Solutions from Thermal Decomposition Products

In no case did the solid, obtained from thermal decomposition of the hydrate, dissolve completely in the organic solvent. Even after repeated extraction, a considerable residue remained. This, in itself, was not of paramount importance since the undissolved material was readily removed by filtration. The following table summarises the results obtained. The symbol (+) is used to indicate that the solid product had dissolved in the solvent to give a solution which was spectroscopically similar to the corresponding solution obtained by metathesis. Where no solution was effected the symbol (o) is used.

Solutions from Thermal Dehydration Products

Solid Product	Solvent	Cr^{3+}	Co^{2+}	Cu^{2+}	Fe^{3+}	Mn^{2+}	Ni^{2+}
ClO_4^-	E	o	+	+	+	+	+
	B	o	o	+	o	o	o
	N	+	+	+	+	+	+
$O_2CCF_3^-$	E	+	+	+	+	+	+
	B	+	o	+	+	+	o
	N	+	+	+	+	+	+
BF_4^-	E	o	+	o	o	o	o
	B	o	o	o	o	o	o
	N	+	+	+	o	+	+

E = Ether
B = Benzene
N = Nitromethane

The spectra of the solutions of some of the decomposition products in nitromethane are compared in the following table with the values obtained from solutions prepared by metathesis, in the region 25,000 - 10,000cm^{-1}. Maxima are quoted in cm^{-1} x 10^{-3}.

Comparison of Spectra of Nitromethane Solutions

Compound	Route	
	Thermal Decomposition	Metathesis
$Cu(ClO_4)_2$	14.4	14.5
$Cu(BF_4)_2$	15.5	15.6
$Co(ClO_4)_2$	18.5	18.5
$Co(O_2C.CF_3)_2$	18.5	18.5
$Ni(O_2C.CF_3)_2$	14.9, 15.6	14.8, 15.6
$Cr(ClO_4)_3$	17.2, 15.2	17.1, 15.2

The remaining thermal decomposition products, not mentioned in the table above, also gave solution spectra which were virtually identical with those obtained from the corresponding solution described in Chapter I.

(b) Solutions from Dehydration Products (2,2 Dimethoxypropane Method)

The solid trifluoroacetates and tetrafluoroborates, obtained by evaporation of the solvent mixture after dehydration using 2,2 dimethoxypropane (2,2 D.M.P.) appeared to retain solvated methanol.

In many instances, the solid product dissolved in ether, benzene and nitromethane only after prolonged shaking. The colours of the solutions were somewhat different from those of the corresponding solutions obtained by metathesis. This was reflected in their visible spectra. A comparison of some of the spectra in the region 25,000 - 10,000 cm^{-1} is given in the table below. Maxima are quoted in $cm^{-1} \times 10^{-3}$.

Comparison of Spectra of Ether and Nitromethane Solutions

Compound	Ether		Nitromethane	
	Route			
	Metathesis	2,2 DMP	Metathesis	2,2 DMP
$Co(BF_4)_2$	-	-	20.0.	20.0.
$Co(O_2C.CF_3)_2$	20.3, 17.8.	20.8, 19.2.	18.5, 17.0.	19.2.
$Ni(BF_4)_2$	-	-	16.7.	20.8.
$Ni(O_2C.CF_3)_2$	24.5, 14.6, 13.5.	15.7, 13.9.	14.9, 13.6.	15.5.
$Cr(O_2C.CF_3)_2$	23.3, 16.3, 14.5.	17.5.	23.3, 17.1, 14.9.	18.8.
$Co(ClO_4)_2$ (X)	-	-	18.5.	18.5.
$Cu(ClO_4)_2$ (X)	-	-	14.5.	14.5.

(X) indicates that the solvent mixture was removed by fractional evaporation as previously described. Attempts to repeat this procedure using benzene as the boiler liquid were less successful.

A precipitate formed in most cases and any colour which appeared in the supernatant liquid was very weak. It may be assumed that addition of benzene caused precipitation of the methanolate complex.

Summary

Alternative methods for the preparation of solutions of transition metal perchlorates, trifluoroacetates and tetrafluoroborates starting from the hydrated compounds have been investigated. This method would be particularly suitable for the trifluoroacetates since the anhydrous compounds can be easily obtained in many cases. For perchlorate and tetrafluoroborate solutions, it has been established that metathesis is the superior method of preparation. Repeated partial evaporation of the perchlorate solutions using nitromethane as solvent met with some success. Methanol, acetone and excess 2,2 dimethoxypropane were reduced to negligible proportions in four or five evaporations. The distillate at this stage showed a single peak on vapour-phase chromatographic analysis. There is no reason why this method could not be applied to the preparation of other strong acid salt solutions in nitromethane.

It would, however, be reasonable to suppose, that the existance of chloroperchlorates, -trifluoroacetates and - tetrafluoroborates would not have been discovered, had the original concept of solution preparation been via the hydrate.

Preparation of Anhydrous Salts from Solutions in Organic Solvents

Attempts were made to obtain anhydrous compounds from the solutions obtained by metathesis. As mentioned previously in this chapter, the removal of organic solvent in contact with perchlorates is a hazardous operation. Evaporation of the solvent from perchlorate solutions was carried out under vacuum using a suitable shield round the sample flask. In general, the solids which resulted were not pure although the infra-red spectra showed a broad absorption in the region 1,100-1000cm^{-1}, indicating the presence of the perchlorate group. Attempts to sublime the solid samples under vacuum also met with little success. It is possible that the solid perchlorate is solvated and removal of the solvent destabilises the compound with subsequent decomposition.

With trifluoroacetates, evaporation of the solvent is a simple task and the operation is without danger. It has been found possible to isolate both chloro- and bistrifluoroacetates of copper (11) from nitro-methane solution. Bis-trifluoroacetates were also obtained for cobalt (11), zinc (11), manganese (11), and nickel (11), and tris-trifluoroacetates for chromium (111) and iron (111).

Analysis figures for iron (II), titanium (III) and vanadium (III) trifluoroacetates were poor. Attempts to purify the solids by recrystallisation were unsuccessful.

No tetrafluoroborate could be isolated in a pure state from nitromethane. Removal of solvent proceeded quite smoothly until the final stages when decomposition occurred. Solids obtained gave poor analysis results indicating that considerable decomposition had taken place.

Experimental

Metal analyses were carried out by normal analytical methods.

Analyses

Copper (II) Chlorotrifluoroacetate

This was prepared by removing the solvent from nitromethane solution prepared by metathesis. A pale blue-green solid was obtained. This was washed with dry petroleum ether and dried at 30° under vacuum. X-ray powder photography was used, to show that this solid contained no copper (II) chloride and was therefore not simply a 1:1 mixture of copper (II) chloride and copper (II) bistrifluoroacetate.

Calculated for $Cu(Cl)O_2C.CF_3$ Cu:30.0% Cl:16.7%

Found Cu: 30.6%, Cl:16.6%.

Copper (II) Bistrifluoroacetate

Addition of the calculated weight of silver trifluoroacetate dissolved in nitromethane, to the solution first prepared by metathesis, precipitated silver chloride. Removal of the solvent and washing as before gave a blue-green compound.

Calculated for $Cu(O_2C.CF_3)_2$ Cu : 21.9%

Cu : 21.7%.

Analysis of the solid samples obtained from cobalt (11) and nickel (11) solutions as first prepared showed that complete conversion to the chloro-trifluoroacetate had not occurred. The chloride analysis corresponded to 70% and 83% chloro-compound present for cobalt and nickel respectively.

Cobalt (11) bistrifluoroacetate

This was obtained as for copper (11) bistrifluoroacetate. Quantitative conversion by silver trifluoroacetate to the bis-compound gave a mauve coloured solid.

Calculated for $Co(O_2C.CF_3)_2$ Co: 20.7%

Found Co: 20.5%

Nickel (11) bistrifluoroacetate

This was obtained as for the cobalt (11) compound. A green solid was obtained.

Calculated for $Ni(O_2C.CF_3)_2$ Ni: 20.6%

Found Ni: 20.5%.

Manganese (11) bistrifluoroacetate

The solution was slightly coloured brown when obtained by metathesis. The solid obtained on evaporation was washed with dry petroleum ether and the residue recrystallised from petroleum ether/nitromethane mixture.

The white crystals obtained were dried under vacuum at 35°C.

Calculated for $Mn(O_2C.CF_3)_2$	Mn : 19.6%
Found	Mn : 19.7%.

Zinc (II) bistrifluoroacetate

This was prepared by removing nitromethane and washing with petroleum ether as previously described.

Calculated for $Zn(O_2C.CF_3)_2$	Zn : 22.4%
Found	Zn : 22.0%.

Iron (III) tristrifluoroacetate

On evaporation of the red solution obtained in nitromethane, deep red crystals of this compound were obtained.

Calculated for $Fe(O_2C.CF_3)_3$	Fe : 14.1%
Found	Fe : 14.5%.

Chromium (III) tristrifluoroacetate

Dark green crystals were obtained by evaporation and washing as before.

Calculated for $Cr(O_2C.CF_3)_3$	Cr : 13.5%
Found	Cr : 13.5%.

Preparation of hydrated perchlorates, trifluoroacetates and perchlorates and anhydrous trifluoroacetates.

The general method of preparation of the hydrates is well established. A slight excess of metal oxide, hydroxide or carbonate was added to the appropriate acid diluted with a little water. (Availability dictated the form of the metal compound used.) The solutions were reduced to low bulk and the crystalline hydrates obtained were recrystallised from water. The hydrated perchlorates, tetrafluoroborates and trifluoroacetates of cobalt (11), copper (11), nickel (11), manganese (11), chromium (111) and iron (111) were prepared in this way.

Vacuum treatment over phosphorus pentoxide for four days converted all of the trifluoroacetates except iron (111) trifluoroacetate from the hydrate to the anhydrous compound. All other hydrates were dried by similar methods.

Analyses

(a) Perchlorates

The hydrated perchlorates, prepared from aqueous solution, analysed to $M(H_2O)_6(ClO_4)_x$, where x = 2.

When x had a value of 3, as in the iron (111) and chromium (111) compounds, decahydrates were formed.

Copper (11) bisperchlorate hexahydrate

Blue crystals.

Calculated for $Cu(H_2O)_6(ClO_4)_2$ Cu : 17.2%

Found Cu : 16.7%.

Cobalt (11) bisperchlorate hexahydrate

Red crystals.

Calculated for $Co(H_2O)_6(ClO_4)_2$ Co : 16.1%

Found Co : 15.8%

Nickel (11) bisperchlorate hexahydrate

Green crystals.

Calculated for $Ni(H_2O)_6(ClO_4)_2$ Ni : 16.1%

Found Ni : 15.7%.

Manganese (11) bisperchlorate hexahydrate

Light pink crystals.

Calculated for $Mn(H_2O)_6(ClO_4)_2$ Mn : 15.1%

Found Mn : 15.2%.

Chromium (111) trisperchlorate decahydrate

Green crystals.

Calculated for $Cr(ClO_4)_3.10\ H_2O$ Cr : 12.1%

Found Cr : 11.4%.

Iron (111) trisperchlorate decahydrate

Lemon crystals.

Calculated for $Fe(ClO_4)_3.10\,H_2O$ Fe : 12.8%

Found Fe : 12.0%.

(b) Tetrafluoroborates

The hydrated tetrafluoroborates analysed to $M(H_2O)_6\ (BF_4)_x$ where x = 2 or 3.

Copper (11) bistetrafluoroborate hexahydrate

Blue crystals.

Calculated for $Cu(H_2O)_6\ (BF_4)_2$ Cu : 18.4%

Found Cu : 18.0%.

Cobalt (11) bistetrafluoroborate hexahydrate

Red crystals.

Calculated for $Co\ (H_2O)_6\ (BF_4)_2$ Co : 17.3%

Found Co : 17.0%.

Nickel (11) bistetrafluoroborate hexahydrate

Green crystals.

Calculated for $Ni(H_2O)_6\ (BF_4)_2$ Ni : 17.2%

Found Ni : 16.8%.

Manganese (II) bistetrafluoroborate hexahydrate

Off-white crystals.

Calculated for $Mn(H_2O)_6(BF_4)_2$	Mn	: 16.5%
Found	Mn	: 16.0%.

Chromium (III) tristetrafluoroborate hexahydrate

Green solid.

Calculated for $Cr(H_2O)_6(BF_4)_3$	Cr	: 12.4%
Found	Cr	: 12.0%.

Iron (III) tristetrafluoroborate hexahydrate

Lemon crystals.

Calculated for $Fe(H_2O)_6(BF_4)_3$	Fe	: 13.2%.
Found	Fe	: 12.7%.

(c) Trifluoroacetates.

With the exception of the iron (III) compound, all trifluoroacetates could be prepared in the anhydrous form.

Copper (II) bistrifluoroacetate (Anhydrous)

Pale blue-green solid.

Calculated for $Cu(O_2C.CF_3)_2$	Cu	: 21.9%
Found	Cu	: 20.9%.

Cobalt (ll) bistrifluoroacetate (Anhydrous)

Mauve solid.

Calculated for $Co(O_2C.CF_3)_2$ Co : 20.7%

Found Co : 20.1%.

Nickel (ll) bistrifluoroacetate (Anhydrous)

Light green powder.

Calculated for $Ni(O_2C.CF_3)_2$ Ni : 20.6%

Found Ni : 20.1%.

Manganese (ll) bistrifluoroacetate (Anhydrous)

White powder.

Calculated for $Mn(O_2C.CF_3)_2$ Mn : 19.6%

Found Mn : 18.9%.

Chromium (lll) tristrifluoroacetate (Anhydrous)

Dark green solid.

Calculated for $Cr(O_2C.CF_3)_2$ Cr : 13.5%

Found Cr : 12.8%.

Iron (lll) tristrifluoroacetate (hydrated)

Brown solid.

Analysed to $Fe(O_2C.CF_3)_3$ 3.8 H_2O.

The hydrated forms were prepared from the anhydrous compounds by allowing to stand in moist air. In calculating the mass of dimethoxypropane to be used

as a dehydrating agent, it was assumed that hexa-hydrates had been formed in all cases.

(2) Dehydration Methods

(a) Thermal Decomposition

The thermal dehydration of the hydrates was carried out on a Stanton Thermogravimetric Balance working at a chart speed of 6 in./hr. Sample weights varied from 0.1 - 0.15g. and the temperature increase rate was ~2°C/min.

Each sample was first tested to destruction. The graph obtained was then examined for inflections related to partial or total removal of water. A second sample was then heated to the temperature corresponding to the point of inflection and that temperature held constant until decomposition was complete. The sample was placed over phosphorus pentoxide in a desiccator which was then evacuated. Each sample so treated was examined for residual co-ordinated water by means of its infra-red spectrum.

(b) Dehydration by 2,2 Dimethoxypropane

Since the reaction of this reagent with water is slightly endothermic, all dehydrations were carried out at 30°C.

An excess (55%) of the dehydrating agent was added to the hydrate and the mixture shaken for two hours. At the end of this time, the solvent mixture was removed under vacuum from the trifluoroacetates and tetrafluoroborates.

Dry nitromethane was added to the perchlorate samples. Approximately half of the total solvent was removed by vacuum distillation and more dry nitromethane added. This was repeated until vapour-phase chromatography showed a single peak corresponding to pure solvent.

CHAPTER IV

Reactions of some Group Vb trihalides with Silver Salts of Strong Acids.

The chemistry of the Group Vb elements, arsenic, antimony and bismuth is indicative of the increase in metallic character with increasing atomic weight. The trihalides of arsenic and, with the exception of the fluoride, of antimony, are covalent. This is confirmed by the low conductivities of these compounds in the liquid phase. Of the bismuth trihalides, only the trifluoride is a salt, the remainder being of an intermediate nature. The chemistry of Group Vb halides has recently been reviewed (138).

The aqueous chemistry of these elements is dominated by the relative ease of hydrolysis of the ions and by the stability of ions of the type MO^{+} which result. Some evidence for the existance of M^{3+} can be drawn from the fact that antimony and bismuth can be precipitated from strong acid solution by hydrogen sulphide. While arsenic (III) sulphide can be precipitated in the same way, the element, in general, shows little tendency to exist as the trivalent cation.

Antimony and bismuth form definite salts (36) especially with strong oxy-acids, the tendency increasing from antimony to bismuth.

These oxy-salts are stable to hydrolysis in strong acid solution but convert to the MO^+ form in weak acids or water.

In anhydrous non-aqueous solvents, the problem of hydrolysis is overcome and stable complexes can be formed. Schmidt (139) prepared dilute solutions of antimony (111) and bismuth (111) nitrates in aceto-nitrile by electrolysis of silver nitrate solutions using the appropriate metal as the anode. By a similar method, the same author prepared solutions of the per-chlorates of the above elements using silver perchlorate as the electrolyte. No mention is made of any attempt to obtain pure solid samples of these oxy-salts. A complex bismuth perchlorate with dioxane, corresponding to the formula $Bi(ClO_4)_3$ 5.5 $C_4H_8O_2$, has been isolated from a solution of Bi_2O_3 in 55% perchloric acid and dioxane (140).

An interesting reaction takes place when bismuth metal is heated with perchloric acid (141). A brown coating appears on the surface of the metal. On removing from the acid and heating further, an explosion occurs leaving a clean but pitted surface. It is recognised that this is a surface phenomenon but its nature is unknown.

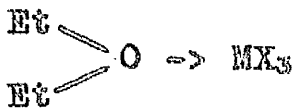
The pentahydrate, $Bi(ClO_4)_3.5H_2O$ can be prepared by treating Bi_2O_3 with 70% perchloric acid and is very sensitive to moisture (142).

Cady and Fujioka (143) reported the preparation of arsenyltrifluoroacetate [$AsO(O_2C.CF_3)$], antimony (111) and bismuth (111) trifluoroacetates using the action of a mixture of trifluoroacetic acid and anhydride on the oxide. The anhydride is used to absorb water produced in the reaction. By removing the solvent, the anhydrous trifluoroacetates could be prepared. When these trifluoroacetates were treated with perchloric acid, partial conversion to the perchlorate was observed in the antimony and bismuth compounds. The arsenyl compound, on reaction with perchloric acid, gave an unidentified colloidal precipitate.

Very recently, the preparation of arsenic trifluoroacetate has been reported (144). The method used was similar to that described above. Arsenious oxide was treated with excess trifluoroacetic anhydride in a sealed tube at room temperature for five days. On breaking the seal and pumping off excess anhydride, a white hygroscopic compound was obtained. This compound sublimed readily.

Little mention is made in the literature of tetrafluoroborates of arsenic, antimony or bismuth in the trivalent state. It might be expected that bismuth (111) would be the most likely to form a tetrafluoroborate. The tetraphenyl '-onium' salts can be obtained for arsenic and antimony by reacting diphenyliodonium tetrafluoroborate with triphenyl arsine or triphenyl stibine respectively (146).

Complexes in which arsenic, antimony and bismuth act as acceptors, electrons being donated by the complexing agent, are well-known. The trihalides dissolve in ether, presumably with the formation of compounds of the formula



Only a small number of compounds of this type are known for arsenic. Petzold (146) obtained salts of organic bases of the type $R_2NH_2(AsCl_4)$, $(R_2NH_2)_2(AsBr_5)$. Arsenic trichloride -pyridine complexes have been known for some time (147).

These have compositions corresponding to the formulae $2AsCl_3.C_5H_5N$, $AsCl_3.C_5H_5N$ and $AsCl_3.2C_5H_5N$. Similar stoichiometries are found in the corresponding bromide and iodide.

In antimony, more numerous examples of acceptor complexes are found. In addition to the ether and pyridine complexes, addition compounds with aromatic hydrocarbons have been reported (36). Thus benzene, toluene and mesitylene form 1:2 or 1:1 complexes presumably by donation of their π electrons to the antimony. The structures of these complexes are not known. Ammine (148), aniline and quinoline (149) complexes of antimony trihalides have also been reported.

Many bismuth complexes with donating species are known. Tertiary amines, aniline and ether complexes have been reported by various authors. In addition, bismuth (and antimony) form very stable chelate 'ato' complexes. The chelation is demonstrated by the stability to hydrolysis of such complexes compared with the simple salts. Compounds of the formulae $M[Sb(OX)_2]$, $M[Bi(OX)_2]$, $M[Sb(SO_4)_2]$ and $M[Bi(SO_4)_2]$ are largely unaffected by moisture or dilution.

In the present work, attempts have been made to prepare anhydrous perchlorates, trifluoroacetates and tetrafluoroborates of trivalent arsenic, antimony and bismuth. The method used was metathesis involving stoichiometric quantities of the anhydrous bromide of the Group Vb element and the anhydrous silver salt of the strong acid.

The anhydrous solvents used were ether and nitromethane. Without exception quantitative yields of silver bromide were recovered.

Attempts to prepare anhydrous tetrafluoroborates corresponding to the formula MX_3 (where X is the strong acid anion) by removal of solvent were largely unsuccessful. Vacuum distillation of ether or nitromethane from tetrafluoroborate solutions produced no solid until most of the solvent had been removed. At this stage, the solution darkened in colour and further evaporation yielded unidentified solids. The dark residue did, however, show a broad absorption in the region 1100-1000 cm^{-1} which may be attributed to the BF_4^- group.

Some success was encountered with the trifluoroacetates. The residue on evaporation was heated in a sublimation apparatus and sublimates obtained in all three cases. The solids were extremely hygroscopic and this made analyses difficult. The infra-red spectra of these solids in the region 1800-650 cm^{-1} are listed in the table below:

Infra-Red Spectra of Trifluoroacetate Sublimates

As	Sb	Bi
1748 (s)	1739 (s)	1661 (s)
1223 (b)	1220 (b)	1212 (b)
1163 (b)	1170 (b)	1163 (s)
855 (s)	866 (s)	862 (s)
797 (s)	800 (s)	800 (s)
733 (s)	727 (s)	725 (s)

While no analytical data is available, it is suggested that these sublimates are the tris-trifluoroacetates. The arsenic compound resembles closely, in physical properties, the white solid described by Emeleus and Dunn (144).

Removal of organic solvents from perchlorate solutions by distillation was not attempted. The ethereal solution obtained after filtration to remove silver bromide was added to a large volume of dry petroleum ether. White solids precipitated in all three cases. The mother liquor was removed by decantation, the residue washed several times with petroleum ether and dried by pumping.

Analysis figures were not satisfactory and did not correspond to the formula $M(ClO_4)_3$. The white residues obtained on precipitation did not redissolve completely in ether. The infra-red spectra showed a strong absorption in the region 1100-1000 cm^{-1} indicating the presence of the ClO_4^- group. It may be reasoned from the above observations that, at some stage in the isolation of the solids, the relative stability of the MO^+ ion results in partial decomposition of the tris-perchlorate, if formed. The removal of the solvating molecule would destabilise the compound and could lead to some decomposition.

Preparation and Infra-red Spectra of Pyridine Complexes

In view of the fact that efforts to prepare the simple strong acid salts of arsenic, antimony and bismuth were unrewarding, it was reasoned that stabilisation of the molecules by the formation of acceptor complexes might lead to compounds which could be isolated. Pyridine was chosen as the donor molecule since pyridine-halide complexes of the above elements were well-known. Solutions of the salts were prepared in ether as previously described. Dry pyridine was added dropwise until a precipitate formed.

Pyridine complexes of all three elements were obtainable using the perchlorate and trifluoroacetate tetrafluoroborate solutions. Analyses for the perchlorate and tetrafluoroborate complexes conformed to the general formula $MX_3 . 3C_5H_5N$ where X is the strong acid anion. Analytical values for the trifluoroacetates were poor. It may be inferred that similar compounds to those mentioned above have been prepared but analysis figures do not confirm this.

The infra-red spectra of the pyridine-trihalide complexes of arsenic, antimony and bismuth have been reported by Watari and Kinumaki (150). Changes in the positions of some of the bands, when comparing the spectrum of co-ordinated pyridine and the free base, are listed. The results obtained are similar to those of Gill et al (151), who recorded the spectra of a number of pyridine complexes and concluded that the major changes which occur on complexing are:-

	Pyridine (free)	Pyridine (complex)
(i)	1578 cm^{-1}	1600 cm^{-1}
(ii)	-	1250 cm^{-1} (w)
(iii)	601 cm^{-1}	625 cm^{-1}
(iv)	403 cm^{-1}	420 cm^{-1}.

(i) A band ~1600 cm^{-1} appears in the pyridine-perchlorates and tetrafluoroborates of all three elements Because of the COO^{-} asymmetrical stretch in the trifluoroacetates, it is not possible to observe this band.

(ii) All the pyridine complexes show a weak band ~1250cm^{-1}.

(iii)(iv) The band ~ 625 cm^{-1} is present in the spectra of all the pyridine complexes. The band at ~ 420cm^{-1} is not well defined probably because it appears at the extreme end of the frequency scale examined (4000 - 400cm^{-1}).

Bands due to anions

(a) Trifluoroacetates

In all three trifluoroacetates, a band due to the asymmetrical stretch of the carboxyl group is observed. The positions of the peaks are given in the following table:

	ν_{as} (COO^{-})
As	1666 cm^{-1}
Sb	1675 cm^{-1}
Bi	1680 cm^{-1}

Complexed pyridine shows three absorptions ~1570, 1480 and 1440 cm^{-1}. The presence of these three bands makes it difficult to select or assign the band due to the

symmetrical COO^{-} stretching vibration which should occur~1450cm^{-1}. The three bands, described in Chapter II, appearing in all trifluoroacetates, are positioned at the following frequencies.

	C-C str.	sym CF_3 def.	$C\begin{matrix}O\\<\\O\end{matrix}$ def.
As	837	801	722
Sb	832	800	720
Bi	836	802	723

All figures in cm^{-1}.

These bands are similar to the corresponding bands obtained with the alkali metal trifluoroacetates described in Chapter II.

(b) Perchlorates and Tetrafluoroborates

The bands observed due to these anions are symmetrical. Some shoulders appear on the low frequency side but these may be attributed to vibrations of the pyridine. The following table shows the bands obtained.

Anion	Perchlorate		Tetrafluoroborate	
Element	ν_3	ν_4	ν_3	ν_4
As	1080 (br)	625 (ms)	1050 (br)	520 (m)
Sb	1080 (br)	625 (ms)	1055 (br)	520 (m)
Bi	1085 (br)	625 (ms)	1100-1030 (v. br.)	520 (m)

All figures in cm^{-1}.

The shape of the peaks obtained from the perchlorate and tetrafluoroborate groups indicate that these are ionic in nature.

EXPERIMENTAL

Preparation of solutions, filtrations and mulling for infra-red examination of solids were carried out in the dry-box. Ether and nitromethane were dried as previously described. Pyridine was dried over molecular sieves and distilled on to molecular sieves. Anhydrous silver perchlorate, trifluoroacetate and tetrafluoroborate were prepared as described in Chapter I.

Arsenic, antimony and bismuth tribromides were prepared by standard literature methods (152) and further purified by vacuum distillation.

Analyses

Arsenic Tribromide

Calculated for $AsBr_3$	:	Br	: 76.2%
Found		Br	: 75.7%.

Antimony Tribromide

Calculated for $SbBr_3$	:	Br	: 66.3%
Found		Br	: 66.7%.

Bismuth Tribromide

Calculated for $BiBr_3$	:	Br	: 53.4%
Found		Br	: 53.0%.

Preparation of Solutions of Strong Acid Salts

The solutions of arsenic, antimony and bismuth perchlorate, trifluoroacetate and tetrafluoroborate were prepared by reacting calculated quantities of silver salt with the tribromide dissolved in ether or nitromethane. The precipitate of silver bromide was filtered off and weighed in order to determine the extent to which reaction had occurred. In all cases the yield was quantitative.

Preparation of Pyridine Complexes

Dry pyridine was added slowly to the ether solutions described above. The pyridine complex which precipitated out was washed with dry petroleum ether and dried by pumping over phosphorus pentoxide.

Analyses

Calculated values are based on a general formula $MX_3 \cdot 3C_5H_5N$ (C= calculated, F = found).

1. Arsenic

	Perchlorate				Tetrafluoroborate		
	%C	%H	%N		%C	%H	%N
C	29.5	2.5	6.9	C	31.5	2.6	7.3
F	28.9	2.9	6.1	F	29.7	2.8	7.0

2. Antimony

	Perchlorate				Tetrafluoroborate		
	%C	%H	%N		%C	%H	%N
C	27.4	2.3	6.4	C	29.1	2.4	6.8
F	25.9	2.4	5.9	F	27.9	2.7	5.9

3. Bismuth

	Perchlorate				Tetrafluoroborate		
	%C	%H	%N		%C	%H	%N
C	24.2	2.0	5.6	C	25.5	2.1	5.9
F	26.9	2.9	4.8	F	23.3	2.7	5.2

REFERENCES

1.	Franklin, E. C. and Kraus, C. A.,	Amer. Chem. J., 1898, 20, 820.
2.	Walden, P.,	Ber., 1899, 32, 2862.
3.	Hill, A. E.,	J. A. C. S., 1921, 43, 254.
4.	Sharp, D. W. A.,	Thesis, Cambridge, 1957.
5.	Sharpe, A. G.,	J. C. S., 1952, 4536.
6.	Braekken, H., and Harang, L.,	Z. Krist., 1930, 75, 538.
7.	Sharpe, A. G.,	'Fluorine Chemistry' Ed. Simons, (Academic Press, N. Y.), 1950.
8.	Blakslee, A. E., and Hoard, J. L.,	J. A. C. S., 1956, 78, 3029.
9.	Mulliken, R. S.,	J. A. C. S., 1952, 74, 811.
10.	Rundle, R. E., and Goring, J. H.,	J. A. C. S., 1950, 72, 5337.
11.	Smith, H. G., and Rundle, R. E.,	J. A. C. S., 1958, 80, 5075.
12.	Taufen, H. J., Murray, M. J., and Cleveland, F. F.,	J. A. C. S., 1941, 63, 3500.
13.	Cromwell, T. M., and Scott, R. L.,	J. A. C. S., 1950, 72, 3825.
14.	Clark, H. C., and O'Brien, R.,	Inorg. Chem., 1963, 5, 1020.

15.	Tildesley, B.D., and Sharpe, A.G.,	Research, 1953, 6, 518.
16.	Orgel, L.E.,	Quart. Rev., 1954, 8, 446.
17.	Andrews, L.J., and Keefer, R.M.,	J.A.C.S., 1952, 74, 640.
18.	Tildesley, B.D., and Sharpe, A.G.	Research, 1954, 7, 98.
19.	Andrews, L.J., and Keefer, R.M., idem.	J.A.C.S., 1949, 71, 2379. ibid. 1950, 72, 3113, 5034.
20.	Chatt, J., Chatt, J., and Duncenson, L.A.,	J.C.S., 1949, 3340. J.C.S., 1953, 2939.
21.	Monnier, G.,	Ann. Chim., 1957, 2(13), 14.
22.	Addison, C.C., and Hathaway, B.J.,	J.C.S., 1958, 3099.
23.	Hathaway, B.J.,	Proc. Chem. Soc., 1958, 344.
24.	Davidson, N.R., and Sutton, L.E.,	J.C.S., 1942, 565.
25.	Swarts, F.,	Bull. Soc. Chim. Belg., 1939, 48, 176.
26.	Spurgeon, W.M.,	Thesis, Michigan, 1941.
27.	Peyronel, G., Belmondi, G., and Vezzosi, I.M.	J.I.N.C., 1958, 8, 577.
28.	Woolf, A.A.,	J.C.S., 1954, 4113.

29.	Hazeldine, R.N., and Kidd, J.M.,	J.C.S., 1954, 4228.
30.	Moss, J.H.,	Thesis, Cambridge, 1955.
31.	Andrews, L.J., and Keefer, R.M., (See also refs. 17, and 19.)	J.A.C.S., 1949, 71, 3644.
32.	Lien, A.P., and McCauley, D.A.,	U.S. Patent 2, 726, 275, 1950.
33.	Warf, J.C.,	J.A.C.S., 1952, 74, 3702.
34.	Heyns, K., and Paulsen, H.,	Angew. Chem., 1960, 72, 349.
35.	Russell, D.R., and Sharp, D.W.A.,	J.C.S., 1961, 4689.
36.	Sidgwick, N.V.,	'The Chemical Elements and their Compounds', (Oxford University Press), 1950.
37.	Sharpe, A.G., and Sharp, D.W.A.,	J.C.S. 1956, 1855, 1858.
38.	Moss, K.,	Thesis, London, 1962.
39.	Eberz, W.F., Welge, H.J., Yost, D.M., and Lucas, H.J.,	J.A.C.S., 1937, 59, 45.
40.	Comyns, A.E., and Lucas, H.J.,	J.A.C.S., 1957, 79, 4839.
41.	Quinn, H.W., and Glew, D.N.,	Can. J. Chem., 1962, 40, 1103.
42.	Belgian Patent	616, 796, Oct. 1962.

43.	I.C.I. Belgian Patent,	621, 065, Feb. 1963.
44.	Baker, B.B.,	Inorg. Chem., 1964, 3(2), 202.
45.	Tropsch, H., and Mattox, W.J.	J.A.C.S., 1935, 57, 1102.
46.	Andrews, L.J., and Keefer, R.M., Keefer, R.M., Andrews, L.J. and Kepner, R.E.,	J.A.C.S., 1948, 70, 3261. J.A.C.S., 1949, 71, 2379, 2381.
47.	Morgan, H.H.,	J.C.S., 1923, 2901.
48.	Comyns, A.E.,	Unpublished work.
49.	Andrews, L.J.,	Chem. Rev., 1954, 54, 713.
50.	Plotnikov, W.A., and Jakubson, S.,	Z.Phys. Chem. 1928, 138, 251.
51.	idem.	ibid. 1930, 147, 227.
52.	Acerete, J.G., and Lacal, Y.R.U.,	Rev. acad. scienc. exact. fys-quim. y nat., Zaragoza, 1954, 9, 117.
53.	Klemm, W., and Tilk, W.	Z. anorg. Chem. 1932, 207, 161, 175.
54.	Garton, G., and Powell, H.M.,	J.I.N.C., 1957, 4, 84.
55.	Woodward, L.A., Garton, G., and Roberts, H.L.,	J.C.S., 1956, 3723.
56.	Woodward, L.A., and Nord, A.A.,	J.C.S., 1956, 3721.
57.	Rundle, R.E., and Corbett, J.D.,	J.A.C.S., 1957, 79, 757.

58.	McCauley, D.A., Shoemaker, B.H., and Lien, A.P.,	Ind. Eng. Chem., 1950, 42, 2103.
	McCauley, D.A., and Lien, A.P.,	J.A.C.S., 1951, 73, 2013.
	idem.	ibid. 1952, 74, 6246.
59.	Gold, V., and Satchell, D.P.N.,	J.C.S., 1955, 3609.
60.	Olah, G., Kuhn, S., and Pavlath, A.,	Nature, 1956, 178, 693.
61.	Winstein, S., and Lucas, H.J.,	J.A.C.S., 1938, 58, 836.
62.	Jander, G., and Krafftczyk, K.,	Z. anorg. Chem. 1955, 282, 121.
63.	Wiberg, E., and Schmidt, M.,	Z. Natur. 1951, 6b, 172.
64.	Evans, W.V., and Lee, F.H.,	J.A.C.S., 1933, 55, 1474.
	idem.	ibid. 1934, 56, 654.
65.	Clifford, A.F., Beachell, H.C., and Jack, W.M.,	J.I.N.C., 1957, 5, 57.
66.	Schwarzenbach, G.,	see Fairbrother, Proc. Int. Conf. on Co-ord. Chem., Amsterdam, 1955.
67.	Willard, H.H., and Kassner, J.L.,	J.A.C.S., 1930, 52, 2391.
68.	Olah, G.A., and Quinn, H.W.,	J.I.N.C. 1960, 14, 295.
69.	Gill, N.S., and Nyholm, R.S.,	J.C.S., 1959, 3997.
70.	Harris, C.M., Nyholm, R.S., and Phillips, D.J.,	J.C.S., 1960, 4379.

71.	Madan, S.K., and Denk, M.M.,	J.I.N.C., 1965, 27, 1049.
72.	Dunn, T.M., and Buffagni, S.,	Nature, 1960, 188, 937.
73.	Baillie, M.J., Brown, D.H., Moss, K., and Sharp, D.W.A.,	Chem. Comm. 1965, 5, 91.
74.	Woolf, A.A., and Emeléus, H.J.	J.C.S., 1949, 2865.
75.	Inorganic Syntheses	Vol.V, Ed. Moeller (McGraw-Hill), 1957, p.153.
76.	Hein, Fr., Farl, H., and Bar, H.,	Ber. 1930, 63, 1418.
77.	Inorganic Syntheses,	Vol.III, Ed. Audrieth, (McGraw-Hill), 1950. p.191.
78.	Inorganic Syntheses,	Vol. VI, Ed.Rochow, (McGraw-Hill), 1960. p.172.
79.	Jørgensen, C.K.,	'Absorption Spectra and Chemical Bonding', (Pergamon Press) 1962.
80.	Ballhausen, C.J.,	'Introduction to Ligand Field Theory', (McGraw-Hill), 1962.
81.	Dunn, T.M.,	in 'Modern Co-ordination Chemistry', Ed. Lewis, J., and Wilkins, R.G., (Interscience) 1960.
83.	Penney, W.G., and Schlapp, R., idem.	Phys. Rev., 1932, 41, 194. ibid. 1932, 42, 666.

84.	Mulliken, R. S.,	J. A. C. S., 1950, 72, 600.
85.	Ilse, F. E., and Hartmann, H.,	Z. Phys. Chem., 1951, 197, 239.
86.	Orgel, L. E.,	'An Introduction to Transition Metal Chemistry. Ligand Field Theory'. (Methuen), 1959.
87.	Hartmann, H., and Schläffer, H. L.,	Z. Phys. Chem., 1951, 197, 116.
88.	Hartmann, H., Schläffer, H. L., and Hansen, K. H.,	Z. anorg. Chem. 1956, 284, 153.
89.	Hathaway, B. J., and Webster, D. E.,	Proc. Chem. Soc., 1963, 14.
90.	Heidt, L. J., Koster, J. F., and Johnson, A. M.,	J. A. C. S., 1958, 80, 6471.
91.	Jørgensen, C. K.,	Acta. Chem. Scand. 1958, 12, 903.
92.	Rabinowich, E., and Stockmeyer, W. H.,	J. A. C. S., 1942, 64, 335.
93.	Kiss, A. v.,	Z. Anorg. Chem. 1940, 244, 99.
94.	Dvir, M., and Low, W.,	Phys. Rev. 1958, 8, 954.
95.	Dreisch, T., and Kallscheuer, O.,	Z. Elektrochem., 1944, 50, 224.
96.	Holmes, O. G., and McClure, D. S.,	J. Chem. Phys. 1957, 26, 1686.
97.	Jørgensen, C. K.,	Acta. Chem. Scand. 1954, 8, 1502.

98.	Liehr, A. D., and Ballhausen, C. J.,	Ann. Phys. (N. Y.), 1958, 3, 304.
99.	Orgel, L. E.,	J. Chem. Phys., 1955, 23, 1004.
100.	Jørgensen, C. K., and Schläffer, H. L.,	J. I. N. C., 1958, 8, 143.
101.	Callery Chemical Co.,	Annual Reports, Feb. 1964, Oct. 1964.
102.	Popov, A. I.,	in 'Technique of Inorganic Chemistry' Vol. I, Ed. Jonassen and Weissberger, (Interscience) 1963.
103.	Hathaway, B. J., and Underhill, A. E.,	J. C. S., 1961, 3091.
104.	idem.	ibid. 1962, 2257.
105.	Bellamy, L. J.,	'The Infra-red Spectra of Complex Molecules' (Methuen), 1958.
106.	Talbot, J. H.,	Acta. Cryst., 1953, 6, 720.
107.	van Niekerk, J. N., and Schoening, F. R. L.	Acta. Cryst. 1953, 6, 227.
108.	Haszeldine, R. N.,	Nature, 1951, 168, 1028.
109.	Nakamoto, K., Morimoto, Y., and Martell, A. E.,	J. A. C. S., 1961, 83, 4528.
110.	Fuson, N., Josien, M. L., Jones, E. A., and Lawson, J. R.,	J. Chem. Phys., 1952, 20, 1627.

111.	Thompson, R.C., and Yawney, D.B.W.,	Can. J. Chem. 1965 43, 1240.
112.	Greenwood, N.N.,	J.C.S., 1959, 3811.
113.	Addison, C.C., Hathaway, B.J., and Logan, N.,	Proc. Chem. Soc. 1958, 51.
114.	Henry, N.,	Thesis, Glasgow, 1965.
115.	Herzog, S., and Kallies, W.,	Z. anorg. Chem., 1964, 329, 83.
116.	Nyholm, R.S.,	Quart. Rev., 1953, 7, 377.
117.	Figgis, B.N., and Lewis, J.,	in 'Modern Co-ordination Chemistry', Ed. Lewis and Wilkins, (Interscience), 1960.
118.	Evans, D.F.,	J.C.S., 1959, 2003.
119.	Kato, M., Jonassen, H.B., and Fanning, J.C.,	Chem. Rev. 1964, 99.
120.	Kagarise, R.E.,	J. Chem. Phys. 1957, 27, 219.
121.	Bellamy, L.J., and Branch, R.F.,	Nature 1954, 173, 635.
122.	Peacock, R.D., and Sharp, D.W.A.,	J.C.S., 1959, 2762.
123.	Perchlorates.	Schumacher (Reinhold) 1960.
124.	Addison, C.C., and Hathaway, B.J.,	Proc. Chem. Soc., 1957, 19.
125.	Rosolovski, V.Ya., Rumyantsev, E.S., and Mal'tseva, N.N.,	Z. Neorgan. Khim., 1963, 8(6), 1332.

126.	Hathaway, B. J., and Underhill, A. E.,	J. C. S., 1960, 648.
127.	West, C. D.,	Z. Krist., 1935, 51, 480.
128.	Hill, A. E., and Miller, F. W.,	J. A. C. S., 1925, 47, 2702.
129.	Marvin, G. G., and Woolaver, L. B.,	Ind. Eng. Chem., Anal. Ed. 1945, 17, 474.
130.	Sharp, D. W. A.,	Advances in Fluorine Chemistry 1960, 1, 66.
131.	Erley, D. S.,	Anal. Chem. 1957, 29, 1564.
132.	Starke, K.,	J. I. N. C., 1959, 11, 77.
133.	Franz, G.,	ibid. 1963, 737.
134.	Meek, D. W., Drago, R. S., and Piper, T. S.,	Inorg. Chem. 1962, 1, 285.
135.	Moore, L. E., Gayhart, R. B., and Bull, W. E.,	J. I. N. C., 1964, 896.
136.	Inhof, V., and Drago, R. S.,	Inorg. Chem. 1965, 4, 427.
137.	Loos, K. R., and Lord, R. C.,	Spectrochim. Acta., 1965, 21(1), 119.
138.	Payne, D. S.,	Quart. Rev. 1961 XV. 2. 173.
139.	Schmidt, H.,	Z. anorg. Chem. 1953, 271, 305.
140.	Golub, A. M., and Baran, A. A.,	Ser. Astron. Fiz. ta Khim, 1961, No. 2, 66.

141.	Nicholson, D.C., and Reedy, J.H.,	J.A.C.S., 1935, 57, 817.
142.	Fichter, F., and Jenny, E.,	Helv. Chim. Acta., 1923, 6, 225.
143.	Cady, G.H., and Fujioka, G.S.,	J.A.C.S., 1957, 79, 2451.
144.	Emeléus, H.J., and Dunn, M.J.,	J.I.N.C., 1966, 27, 269.
145.	Makarova, L.G., and Nesmeyanov, A.N.,	Izvest. Akad. Nauk. S.S.S.R. Otdel Khim. Nauk 1954, 617.
146.	Petzold, W.,	Z. anorg. Chem. 1933, 214, 355.
147.	Dafert, O., and Melinski, Z.A.,	Ber. 1926, 59, 783.
	Gibson, C.S., Johnson, J.D.A., and Vining, D.C.,	J.C.S., 1930, 1710.
	Montignie, E.,	Bull. Soc. Chim. Fr. 1935, 2, 1365.
	Shirey, W.B.,	J.A.C.S. 1930, 52, 1720.
148.	Deherain, P.P.,	Comptes Rendus, 1861, 52, 735.
149.	Schiff, H.,	Annali. 1864, 131, 116.
150.	Watari, F., and Kinumaki, S.,	Sci. repts. Res. Inst., Tohoku Univ., 1961, Ser. A.13, 330.
151.	Gill, N.S., Nuttall, R.H., Scaife, D.E., and Sharp, D.W.A.,	J.I.N.C. 1961, 18, 79.
152.	Gmelins Handbuch.	No.17 - p.392. No.18 - p.471. No.19 - p.151.